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Petroleum

STOPPING
WATER POLLUTION
AT ITS SOURCE

MISA

Municipal/Industrial Strategy for Abatement

EFFLUENT MONITORING REGULATIONS
FOR THE
PETROLEUM REFINING SECTOR

JULY 1988

Ontario

Ministry
of the
Environment

Hon. Jim Bradley
Minister

EFFLUENT MONITORING REGULATIONS
FOR THE
PETROLEUM REFINING SECTOR

June 1988

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EXECUTIVE SUMMARY

The Municipal/Industrial Strategy for Abatement (MISA) is Environment Ontario's program to reduce the discharge of toxic contaminants to Ontario's waterways. Under MISA, dischargers will be required to monitor and report on the contaminants present in their effluent streams. This information will be used to set legal discharge limits requiring reductions in toxic discharges to the level attainable with the best available pollution control technology which is economically achievable. The ultimate goal of the MISA program is the virtual elimination of persistent toxic contaminants from all discharges into Ontario's waterways.

This document contains all legal monitoring requirements for Ontario's petroleum refining sector. These requirements are specified in two regulations, "Ontario Regulation 358/88: Effluent Monitoring - General" and "Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector". Both regulations are issued under the Ontario Environmental Protection Act (Section 136).

"Ontario Regulation 358/88: Effluent Monitoring - General" provides the technical and scientific methodologies for monitoring which are applicable to all dischargers under MISA. In particular, the regulation specifies the principles of sampling, analysis, flow measurement and procedures for toxicity testing. The general regulation also states the two types of reporting requirements industry must follow. An initial report is necessary to provide background information on the plant site and on the equipment and laboratories that will be used to carry out regulatory monitoring requirements. A monitoring report is required at specified intervals to report on analytical results and flow measurement data.

"Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector" states the chemical monitoring, toxicity testing, flow measurement, and reporting requirements that each refinery must meet. The petroleum refining sector regulation comes into force on December 1, 1988, with the exception of the reporting requirements, which become effective on September 1, 1988. Ontario Regulation 359/88 states that sampling points must be established within each refinery on every process, emergency overflow, once-through cooling water, and stormwater effluent stream. Routine chemical monitoring requirements, which include daily, thrice weekly, and quarterly frequencies, are provided in the text of the regulation and the specific contaminants to be monitored, up to 148 conventional pollutants, metals, and organic contaminants, are presented in accompanying schedules in a tabular format. In addition, the regulation requires toxicity testing using both rainbow trout and *Daphnia magna*. Flow measurement protocols applicable to each effluent

stream are also provided. Finally, the petroleum refining sector regulation states the reporting and record-keeping requirements each refinery must follow, throughout the duration of the monitoring regulation.

Explanatory notes follow each regulation, and are provided to amplify and explain the legal text. The order of the explanatory notes corresponds to the order of the regulations.

Part Two of this document presents a discussion of the MISA approach to effluent monitoring. The first chapter addresses the environmental background to MISA and the main features of the program.

Chapter two discusses the role of monitoring in achieving the program's goal of the virtual elimination of persistent toxic substances. Details are provided on the Ministry's monitoring strategy, the effluent monitoring priority pollutants list, and the pre-regulation monitoring programs. The principles of monitoring, such as sampling frequencies for specific effluent streams, and the rationale for all monitoring requirements are presented.

Chapter three describes the petroleum refining sector in terms of raw materials used, products, refinery processes, wastewater sources, and the composition and treatment of refinery effluents.

The petroleum refining sector in Ontario consists of seven plants, six of which are conventional petroleum refineries with total annual sales of 24 billion litres, and one which is a petroleum-based producer of primary petrochemicals with a capacity of 1.3 billion kilograms. Information about each refinery is given, including age and location, production capacities, processes used, and on-site treatment.

The final chapter of Part Two provides a technical rationale for refinery monitoring requirements, including why specific parameters were chosen for each monitoring frequency. The economic implication of the monitoring requirements is also discussed.

This document represents the culmination of over two years of effort on the part of the Ministry, industry, and the public. The public review process was a key component in the development of both the general and petroleum refining regulations, and will continue to form a significant part of MISA regulations development. Draft versions of both regulations were released for public review in July of 1987 and the Ministry received 35 submissions from across the province. In addition to public review, both regulations were reviewed by the MISA Advisory Committee, which is a committee made up of environmental experts external to the Ministry who provide advice to the Minister on the contents of the regulations.

PART ONE: THE REGULATIONS

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ONTARIO REGULATION 358/88

under the Environmental Protection Act

EFFLUENT MONITORING - GENERAL

OFFICE CONSOLIDATION

THIS EDITION IS PREPARED FOR PURPOSES OF CONVENIENCE ONLY, AND FOR ACCURATE REFERENCE RECOURSE SHOULD BE HAD TO THE OFFICIAL VOLUMES OR THE ONTARIO GAZETTE.

Definitions

1. In this Regulation,

"analytical method detection limit" or "MDL" means the minimum concentration of a parameter necessary to imply its presence in a sample with a level of confidence greater than 99 per cent and calculated according to the procedure described in the Ontario Ministry of the Environment publication entitled "Estimation of Analytical Method Detection Limits (MDL)" dated May, 1988;

"analytical run" means a group of samples processed together through each step in an analytical procedure;

"automatic flow proportional composite sampling device" means a piece of equipment that is capable of operating continuously and automatically adjusting, at time intervals not exceeding thirty minutes, either the volume of effluent sub-samples or the time interval between the collection of sub-samples, to the rate of flow in the effluent stream;

"characterization" means the analysis of a sample to identify and quantify all of the parameters in Schedule 1;

"combined effluent" means any intentional combination of process materials, process effluent or waste disposal site effluent with cooling water;

"combined effluent sampling point" means a point in a combined effluent stream situated,

(a) before the place of discharge to a surface watercourse,

(b) after final treatment, and

(c) upstream of any significant contaminant masking or significant dilution by any other effluent;

"combined effluent stream" means an open or closed channel through which combined effluent flows;

"composite sample" means a volume of effluent made up of three or more sub-samples that have been combined automatically or manually or obtained from a slip stream to an on-line analyzer;

"cooling water" means water that is used in an industrial process for the purpose of removing heat and that is not intended to come into contact with process materials;

"direct discharger" means the owner or person in occupation or having the charge, management or control of a plant that discharges contaminated or potentially contaminated effluent to a surface watercourse but does not discharge that effluent solely to a publicly owned sewage works;

"Director", in respect of obligations on a direct discharger, means a director appointed under section 4 of the Environmental Protection Act and responsible for the region in which the direct discharger's plant is located;

"duplicate sample" means one of two samples collected at a sampling point at the same time in a manner that minimizes differences between the samples;

"effluent" means any liquid and associated material discharged to a surface watercourse;

"effluent stream" means an open or closed channel through which effluent flows;

"emergency overflow" means a diversion of effluent that by-passes a sampling point ordinarily used for that effluent;

"emergency overflow sampling point" means a point in an emergency overflow effluent stream situated,

(a) before the place of discharge to a surface watercourse, and

(b) upstream of any significant contaminant masking or significant dilution by other effluent;

"fluorocarbon resin" means polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA) resins, chlorotrifluoroethylene (CTFE) or copolymers of ethylene with tetrafluoroethylene (ETFE) or with chlorotrifluoroethylene (ECTFE);

"grab sample" means a volume of effluent of at least 100 millilitres which is collected over a period not exceeding fifteen minutes and immediately transferred to the appropriate laboratory sample container set out in Column 2 of Schedule 2;

"initial report" means a report required by a Sectoral Effluent Monitoring Regulation to be submitted by a direct discharger to the Director before the other monitoring requirements of that Regulation come into force;

"method blank sample" means an uncontaminated sample of distilled water processed through an entire analytical procedure;

"once-through cooling water" means cooling water that has been circulated once through heat transfer equipment;

"once-through cooling water effluent stream" means an open or closed channel through which once-through cooling water flows;

"once-through cooling water sampling point" means a point in a once-through cooling water effluent stream situated before the place of discharge to a surface watercourse;

"on-line analyzer" means a device used for the continuous sampling and analysis of effluent for pH, specific conductance or dissolved organic carbon (DOC);

"operating day" means the length of time in a twenty-four hour period during which a plant is discharging effluent;

"plant" means an industrial facility and the developed property and waste disposal sites associated with that facility;

"precision" means the degree of variation observed among a set of results obtained from repeated measurements;

"primary flow measuring device" means a piece of equipment that produces a range of measurements specific to the flow at a given location or set of locations;

"process effluent" means any effluent from a plant that is contaminated or potentially contaminated through contact by design with any industrial process;

"process effluent sampling point" means a point in a process effluent stream situated,

(a) before any place of discharge to a surface watercourse,

(b) after final treatment, and

(c) upstream of any significant contaminant masking or significant dilution by any other effluent;

"process effluent stream" means an open or closed channel through which process effluent flows;

"process materials" means raw materials, manufacturing intermediates, products or by-products of an industrial process;

"quality control" means the procedures undertaken by or on behalf of a direct discharger to ensure that the data produced are generated within known probability limits of accuracy and precision;

"quarter" means a period of three months beginning on the first day of January, April, July or October;

"replicate sample" means one of at least two aliquots removed from a single sample container for any or all parameters in a specific analytical test group in a manner that minimizes differences between the aliquots;

"sample" means a collected volume of effluent and includes a composite sample or one or more grab samples;

"sampling point" means a point in an effluent stream at which a sample is collected;

"secondary flow measuring device" means a device or combination of devices that converts information from sensors on a primary flow measuring device into flow data according to the characteristics of the primary flow measuring device;

"Sectoral Effluent Monitoring Regulation" means a regulation under the Environmental Protection Act that sets out effluent monitoring requirements in respect of an industrial sector;

"spiked method blank sample" means a method blank sample to which a certain recorded quantity of a standard solution is added;

"spiked sample" means an effluent sample to which a certain recorded quantity of a standard solution is added by a member of the staff of an analytical laboratory or other qualified person;

"standard reference material" means a material that is certified to contain a certain concentration of a specific analyte and is obtained from the United States National Bureau of Standards, the United States Environmental Protection Agency or an equivalent supplier;

"standard solution" means a solution for which the concentration has been validated against a standard reference material, where available, and that has been prepared by dissolving a certain recorded quantity of one or more chemicals of certain recorded purity into contaminant-free water or other appropriate solvent;

"storm event" means a period of precipitation in a twenty-four hour span,

(a) in which rainfall exceeds five millimetres, as indicated by an on-site rain gauge or an Environment Canada meteorological station located within two kilometres from the plant,

(b) separated from the previous period of precipitation by a minimum of six hours, and

(c) that causes a discharge to a surface watercourse through an effluent stream;

"storm water" means contaminated or potentially contaminated run-off from a storm event that,

(a) results from precipitation on the developed areas of a plant, and

(b) discharges to a surface watercourse through an effluent stream;

"storm water effluent stream" means an open or closed channel through which storm water flows;

"storm water sampling point" means a point in a storm water effluent stream situated before the place of discharge to a surface watercourse;

"surface watercourse" means any lake, river, pond, stream, reservoir, swamp, marsh or surface drainage works;

"variable flow" means the flow of a process effluent that varies by more than plus or minus 15 per cent from the daily mean flowrate, for more than 150 minutes per operating day for more than eighteen operating days in a six month period;

"waste disposal site effluent" means any liquid that percolates through or runs off a waste disposal site and is collected for discharge or is discharged to a surface watercourse.

Purpose and Application

2.-(1) The purpose of this Regulation is to prescribe common sampling, analysis, toxicity testing, flow measurement, recording and reporting requirements for all Sectoral Effluent Monitoring Regulations.

(2) This Regulation applies only in respect of monitoring obligations, including sampling, analysis, toxicity testing, flow measurement, recording and reporting obligations, under a Sectoral Effluent Monitoring Regulation.

(3) In the event of conflict between this Regulation and a Sectoral Effluent Monitoring Regulation, the latter prevails.

Sampling Requirements

3.-(1) Samples shall be collected at a location along and at a point in an effluent stream that is characteristic of the effluent in that stream.

(2) Each sample that is submitted to an analytical laboratory shall be prepared using the appropriate laboratory sample container, container pre-treatment and sampling precautions specified in Columns 2, 3 and 4 of Schedule 2.

(3) Each grab sample shall be collected,

(a) directly from an open effluent stream at a point of complete mixing;

(b) manually through a valve from a pipe running full; or

(c) using a sampling device that does not alter the volatile organics and sulphide characteristics of the sample.

(4) Subject to subsections (5), (7) and (8), each sample collected from a process effluent sampling point or from a combined effluent sampling point shall be a composite sample collected over a twenty-four hour period by,

(a) using an automatic flow proportional composite sampling device;

(b) manually collecting a minimum of eight grab samples at equal time intervals and combining them in proportion to flow;

(c) using an automatic sampling device that collects and combines equal volume sub-samples at equal time intervals not exceeding fifteen minutes; or

(d) manually collecting a minimum of eight grab samples at equal time intervals and combining them in equal volumes.

(5) If a report on flow variability required to be submitted to the Director by a Sectoral Effluent Monitoring Regulation establishes that there is variable flow at any process effluent sampling point, each sample collected from that sampling point after three months from the date of submission of the report shall be collected only in accordance with clause (4)(a) or (b).

(6) Subject to subsections (7) and (8), each sample collected from a once-through cooling water sampling point shall be collected,

(a) according to clause (4)(a), (b), (c) or (d); or

(b) by manually collecting and combining three equal volume grab samples taken at intervals of at least six hours over a twenty-four hour period.

(7) Where a sample is collected from a process effluent sampling point, a combined effluent sampling point or a once-through cooling water sampling point for analysis for parameters in analytical test groups 15 to 18 in Schedule 1, it shall consist of three equal volume grab samples taken at intervals of at least six hours over a twenty-four hour period and combined in the laboratory immediately prior to analysis.

(8) Grab samples collected under subsection (7) for analysis for parameters in analytical test groups 16 to 18 in Schedule 1 shall be combined in a purge vessel.

(9) Each sample collected from a storm water sampling point, an emergency overflow sampling point or a discharge of waste disposal site effluent shall be collected,

(a) according to clause (4) (a), (b), (c) or (d); or

(b) by taking one grab sample.

(10) Clause (9)(a) does not apply to the collection of samples for analysis for parameters in analytical test groups 15 to 18 in Schedule 1.

(11) Composite samples to be analyzed for parameters in analytical test groups 2, 14 and 25 in Schedule 1 shall be collected in separate laboratory sample containers as specified in Column 2 of Schedule 2, and in the case of composite samples to be analyzed for parameters in analytical test groups 2 and 14, preservatives as specified in Column 6 of Schedule 2 shall be added to the sample container prior to sampling.

(12) The wettable surfaces of all sampling equipment used for the collection of samples shall be made of,

(a) fluorocarbon resins, glass or stainless steel for samples that are to be analyzed for parameters in analytical test groups 12, 14 and 16 to 27 in Schedule 1; and

(b) fluorocarbon resins, glass, stainless steel, high or low density polyethylene, polyethylene terephthalate, polystyrene or polypropylene for samples that are to be analyzed for parameters in analytical test groups 1 to 11, 13 and 15 in Schedule 1.

(13) Despite subsection (12), a short section of surgical grade silicone rubber tubing shall be used in peristaltic pump heads or pinch clamps for all automatic sampling devices which use such pumps.

(14) All sample containers and wettable surfaces of the sampling equipment shall be clean so as not to contaminate the sample with any of the parameters in the analytical test groups for which the analysis is to be performed.

(15) Each composite sample collected for the analysis of more than one analytical test group in Schedule 1 shall be continuously mixed while being transferred into the appropriate laboratory sample containers specified in Column 2 of Schedule 2.

(16) The volume of all samples submitted to the laboratory for analysis shall be at least the prescribed minimum sample volume for each analytical test group set out in Column 5 of Schedule 2.

(17) All samples and sub-samples shall be placed without delay in an environment cooled to below 10 degrees Celsius but above the freezing point of the sample, and stored within that temperature range until analyzed.

(18) Subject to subsection (19), samples shall be preserved upon collection without delay, according to the preservation method specified for each analytical test group in Column 6 of Schedule 2.

(19) Samples referred to in subsection (15) shall be preserved without delay following the transfer.

(20) Samples shall be labelled, coded or packaged in a way that identifies them and shall be delivered as soon as practicable to an analytical laboratory.

(21) Each sample shall be analyzed within the times specified in Column 7 of Schedule 2.

(22) Persons engaged in effluent sampling or in the maintenance of sampling equipment shall be competent in those operations.

(23) All sampling devices shall be equipped in a manner that permits, at any time,

(a) safe access;

(b) inspection; and

(c) sampling in the manner normally employed by the direct discharger to satisfy the requirements of a Sectoral Effluent Monitoring Regulation,

by a provincial officer.

Analytical Requirements

4.-(1) Each analytical method shall,

(a) be carried out by competent laboratory personnel in a properly equipped and maintained laboratory environment;

(b) meet generally accepted principles of good laboratory practice and quality control;

(c) be appropriate to the type of sample to be analyzed;

(d) identify the target parameter or parameters;

(e) maximize the recovery of target parameters from effluent samples and allow quantification of recovery levels, where applicable; and

(f) accurately quantify the concentration of the parameter or parameters at and above the relevant analytical method detection limits in spiked method blank samples.

(2) Samples shall be analyzed using,

(a) the applicable sample preparation method principles set out in Column 3 of Schedule 3;

(b) the applicable instrumental measurement method principles set out in Column 4 of Schedule 3 or the alternate instrumental measurement method principles set out in Column 5 of Schedule 3; and

(c) only methods for which the analytical method detection limit does not exceed the applicable maximum analytical method detection limit, if any, specified for the applicable parameter in Column 6 of Schedule 3.

(3) Despite clause (2)(b), samples collected for characterization shall not be analyzed using the alternate instrumental measurement method principles set out in Column 5 of Schedule 3.

(4) All analytical measurement systems shall be calibrated in the following manner:

1. Calibration standards shall be validated using standard reference material where available.
2. A calibration curve of concentration, weight or pH units, as appropriate, versus instrument response shall be established within the range normally encountered in typical samples.
3. Except for analytical test groups 3, 7 and 8 in Schedule 1, samples may be diluted or concentrated to permit measurement within the concentration range established by the calibration curve.
4. Control limits shall be established for daily calibration.
5. The method blank sample, where applicable, shall be shown to fall within control limits and the analytical results adjusted accordingly.
6. In the event that the requirements of paragraph 5 are not met, the samples analyzed in the same analytical run as the method blank sample shall be re-analyzed or a new set of samples shall be collected and analyzed.

(5) The analytical results for each sample from an analytical run shall be corrected for the method blank sample result, where applicable, before the results are reported.

(6) Subject to subsections (7) to (9), at least one of each of the following quality control samples shall be analyzed three times in the course of processing each analytical run, each time to precede the analysis of approximately one-third of the samples in the run:

1. A randomly selected replicate sample, or where the sample volume is insufficient, a randomly selected duplicate sample.

2. A method blank sample.

3. A spiked method blank sample containing all parameters to be analyzed for in the course of the run.

4. A spiked sample containing all parameters to be analyzed for in the course of the run.

(7) Where samples in an analytical run are to be analyzed for parameters in analytical test groups 5b, 7, 8, 11 and 25 in Schedule 1, the quality control samples specified in paragraphs 3 and 4 of subsection (6) need not be analyzed.

(8) Where samples in an analytical run are to be analyzed for parameters in analytical test group 3 in Schedule 1, the quality control samples specified in paragraphs 2, 3 and 4 of subsection (6) need not be analyzed.

(9) Where there are less than twenty-eight samples in an analytical run, the quality control samples required by subsections (6), (7) and (8) shall be analyzed before the processing of any samples and after the processing of fourteen samples in the run, instead of at the times specified in subsection (6).

(10) Where an on-line analyzer is used on an effluent stream, clauses 1(a) and (b), subsection (3), paragraphs 3, 5 and 6 of subsection (4) and subsections (5) to (9) do not apply.

(11) Where an on-line analyzer is used on an effluent stream, it shall be calibrated and maintained at a frequency that accords with good operating practice or the manufacturer's recommendations, whichever is more rigorous.

(12) Where an on-line analyzer is used on an effluent stream, samples must be collected from that stream at least once in each month in accordance with subsection 3(4) and analyzed in a laboratory for the parameters for which the on-line analyzer is monitoring.

Toxicity Testing

5.-(1) Each fish toxicity test shall be performed according to the procedure described in the Ontario Ministry of the Environment publication entitled "Protocol to Determine the Acute Lethality of Liquid Effluents to Fish" dated July, 1983.

(2) Each Daphnia magna acute lethality toxicity test shall be performed according to the procedure described in the Ontario Ministry of the Environment publication entitled "Daphnia magna Acute Lethality Toxicity Test Protocol" dated April, 1988.

(3) Each sample collected for the purpose of performing a fish toxicity test shall consist of not less than eighty litres of effluent.

(4) Each sample collected for the purpose of performing a Daphnia magna acute lethality toxicity test shall consist of not less than five litres of effluent.

(5) Each sample collected for the purpose of performing both a fish toxicity test and a Daphnia magna acute lethality toxicity test shall consist of not less than eighty litres of effluent.

(6) Each toxicity test sample shall be thoroughly mixed prior to testing and, where a sample is required to be collected for both Daphnia magna acute lethality toxicity testing and fish toxicity testing, a sample for Daphnia magna acute lethality toxicity testing shall be withdrawn from the mixed sample.

(7) All containers used to collect toxicity test samples shall be made of stainless steel, glass or fluorocarbon resins, or shall be lined with new food grade polyethylene or new food grade polypropylene.

(8) All sample containers and wettable surfaces of sampling equipment used for toxicity testing shall be clean and non-toxic.

(9) Each toxicity test sample container shall be filled as fully as is practicable with the sample, and shall then be sealed.

(10) No preservatives may be added, or alterations made, to any toxicity test sample.

(11) Each toxicity test shall be initiated within five days after sampling and, if more than forty-eight hours elapses between collecting a sample and testing it, the sample shall be placed in an environment cooled to between 5½ and 15½ Celsius and stored within that temperature range until tested.

Flow Measurement

6.-(1) Where a direct discharger is required to measure the flow of a process effluent stream, that flow shall be continuously measured using methods and devices installed at the stream capable of accuracy to within plus or minus 5 per cent of the actual flow for the primary flow measuring device and plus or minus 2 per cent of full scale flow for the secondary flow measuring device, for the design range of the flow measuring system.

(2) Where a direct discharger is required to measure the flow of a combined effluent stream, that flow shall be continuously measured using methods and devices installed at the stream capable of accuracy to within plus or minus 20 per cent of the actual flow.

(3) Where a direct discharger is required to measure or estimate the flow of an effluent stream at the time of each sampling and the sampling is done in accordance with clause 3(4) (a), (b), (c) or (d), that flow shall be measured or estimated at least three times over the twenty-four hour sampling period, at intervals of at least six hours.

(4) Methods, devices or calculations for the measurement or estimation of the flow of a once-through cooling water effluent stream, a storm water effluent stream, an emergency overflow effluent stream or a discharge of waste disposal site effluent shall be capable of accuracy to within plus or minus 20 per cent of the actual flow.

(5) All secondary flow measuring devices shall be field calibrated before the collection of the first set of samples required to be collected under a Sectoral Effluent Monitoring Regulation and the calibration shall be verified at regular intervals not exceeding one year.

(6) All flow measuring devices shall be equipped so as to enable safe access and inspection by a provincial officer at any time.

(7) All flow measuring devices shall be installed, maintained and calibrated according to good operating practices or the recommendations of the manufacturer, whichever is more rigorous.

Reporting

7.-(1) Each initial report submitted by a direct discharger to the Director shall contain the following information:

1. A plot plan or plans of the direct discharger's plant showing the location of all processing areas, effluent streams from all developed on-site and off-site areas, intakes, emergency overflows, storm drainage areas, points of effluent discharge to surface watercourses, sampling points, sampling devices and flow measuring devices.

2. A simplified overview block diagram of the plant with associated text detailing the raw materials, products and wastes, with the Chemical Abstract Service (CAS) numbers of the active ingredients where available.

3. A list of the types and quantities of chemicals added to once-through cooling water by the direct discharger in the previous calendar year, specifying the trade names or chemical names and Chemical Abstract Service (CAS) numbers of the active ingredients where available.

4. A description of sampling devices to be used and their locations and a listing of laboratory sample containers, laboratory container pre-treatments and preservation methods to be used.

5. A description of any on-line analyzers to be used and their locations and a description of calibration procedures and frequencies.

6. A description of flow measurement methods and devices to be used and documentation of the initial calibration of those devices.

7. A listing of the maximum rated flow capacity for each flow measuring device to be used.

8. A description of rain gauging devices to be used, their locations and the rain gauging methods to be used.

9. The names and addresses of the laboratories that the direct discharger anticipates will carry out the analytical and toxicity test procedures.

10. A listing of the sample preparation and instrumental measurement method principles and analytical method detection limits to be used in the laboratories.

(2) The results of all analyses required to be reported to the Director by a Sectoral Effluent Monitoring Regulation shall be reported in writing signed by the direct discharger and on a floppy diskette or in an equivalent electronic format acceptable to the Director,

(a) within thirty days after the end of the month in which samples were collected on a daily, weekly or three times weekly basis;

(b) within sixty days after the day on which samples were collected on a monthly or quarterly basis, except for samples collected for the analysis of the parameters in the analytical test group numbered 24 in Schedule 1; and

(c) within ninety days after the day on which samples were collected for characterization or for the analysis of the parameters in analytical test group 24 in Schedule 1.

(3) All results of analyses required to be reported by a Sectoral Effluent Monitoring Regulation that fall below the analytical method detection limits calculated by the laboratory performing the analysis shall be reported as the calculated MDL prefixed by the symbol "<" and accompanied by the remark code "<DL" in the report required by subsection (2).

(4) Data collected using an on-line analyzer and required to be reported by a Sectoral Effluent Monitoring Regulation shall be reported as daily minimum, maximum and mean values.

(5) Flow measurement information required to be reported by a Sectoral Effluent Monitoring Regulation shall be reported to the Director in writing signed by the direct discharger and on a floppy diskette or in an equivalent electronic format acceptable to the Director.

(6) Flow measurement information required to be recorded from a process effluent stream shall be reported as,

(a) the total volume of effluent discharged per day where sampling from that stream is done in accordance with clauses 3(4)(a) or (b); or

(b) the maximum, minimum and mean flows per day where sampling from that stream is done in accordance with clauses 3(4)(c) or (d).

(7) Flow measurement information required to be recorded from a combined effluent stream, a once-through cooling water effluent stream, a storm water effluent stream, an emergency overflow effluent stream or a discharge of waste disposal site effluent shall be reported as the total volume of effluent discharged per day.

LEGEND FOR SCHEDULES

#	number
°C	degrees Celsius
g/L	grams per litre
h	hour
L	litre
mg	milligram
mg/L	milligrams per litre
min. sam. vol.	minimum sample volume
mL	millilitre
N	normal
N/A	not applicable
µg/L	micrograms per litre
µS/cm	microsiemens per centimetre
4AAP	4-amino antipyrine method

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS

ANALYTICAL TEST GROUP #	NAME	PARAMETERS
1	Chemical Oxygen Demand	Chemical oxygen demand (COD)
2	Total cyanide	Total cyanide
3	Hydrogen ion (pH)	Hydrogen ion (pH)
4a	Nitrogen	Ammonia plus Ammonium Total Kjeldahl nitrogen
4b	Nitrogen	Nitrate + Nitrite
5a	Organic carbon	Dissolved organic carbon (DOC)
5b	Organic carbon	Total organic carbon (TOC)
6	Total phosphorus	Total phosphorus
7	Specific conductance	Specific conductance
8	Suspended solids	Total suspended solids (TSS) Volatile suspended solids (VSS)
9	Total metals	Aluminum Beryllium Cadmium Chromium Cobalt Copper Lead Molybdenum Nickel Silver Thallium Vanadium Zinc
10	Hydrides	Antimony Arsenic Selenium
11	Chromium (Hexavalent)	Chromium (Hexavalent) (NOTE 1)
12	Mercury	Mercury
13	Total alkyl lead	Tetra-alkyl lead (NOTE 2) Tri-alkyl lead (NOTE 2)

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS

ANALYTICAL TEST GROUP #	NAME	PARAMETERS
14	Phenolics (4AAP)	Phenolics (4AAP)
15	Sulphide	Sulphide
16	Volatiles, Halogenated	1,1,2,2-Tetrachloroethane 1,1,2-Trichloroethane 1,1-Dichloroethane 1,1-Dichloroethylene 1,2-Dichlorobenzene 1,2-Dichloroethane (Ethylene dichloride) 1,2-Dichloropropane 1,3-Dichlorobenzene 1,4-Dichlorobenzene Bromoform Bromomethane Carbon tetrachloride Chlorobenzene Chloroform Chloromethane Cis-1,3-Dichloropropylene Dibromochloromethane Ethylene dibromide Methylene chloride Tetrachloroethylene (Perchloroethylene) Trans-1,2-Dichloroethylene Trans-1,3-Dichloropropylene Trichloroethylene Trichlorofluoromethane Vinyl chloride (Chloroethylene)
17	Volatiles, Non-Halogenated	Benzene Ethylbenzene Styrene Toluene o-Xylene m-Xylene and p-Xylene (NOTE 3)
18	Volatiles, Water Soluble	Acrolein Acrylonitrile

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS

ANALYTICAL TEST GROUP		PARAMETERS
#	NAME	
19	Extractables, Base Neutral	Acenaphthene
		5-nitro Acenaphthene
		Acenaphthylene
		Anthracene
		Benz(a)anthracene
		Benzo(a)pyrene
		Benzo(b)fluoranthene
		Benzo(g,h,i)perylene
		Benzo(k)fluoranthene
		Camphene
		1-Chloronaphthalene
		2-Chloronaphthalene
		Chrysene
		Dibenz(a,h)anthracene
		Fluoranthene
		Fluorene
		Indeno(1,2,3-cd)pyrene
		Indole
		1-Methylnaphthalene
		2-Methylnaphthalene
		Naphthalene
		Perylene
		Phenanthrene
		Pyrene
		Benzylbutylphthalate
		Bis(2-ethylhexyl)phthalate
		Di-n-butylphthalate
		4-Bromophenyl phenyl ether
		4-Chlorophenyl phenyl ether
		Bis(2-chloroisopropyl)ether
		Bis(2-chloroethyl)ether
		2,4-Dinitrotoluene
		2,6-Dinitrotoluene
		Bis(2-chloroethoxy)methane
		Diphenylamine (NOTE 4)
		N-Nitrosodiphenylamine (NOTE 4)
		N-Nitrosodi-n-propylamine

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS

ANALYTICAL TEST GROUP		PARAMETERS
#	NAME	
20	Extractables, Acid (Phenolics)	2,3,4,5-Tetrachlorophenol 2,3,4,6-Tetrachlorophenol 2,3,5,6-Tetrachlorophenol 2,3,4-Trichlorophenol 2,3,5-Trichlorophenol 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol 2,4-Dimethylphenol 2,4-Dinitrophenol 2,4-Dichlorophenol 2,6-Dichlorophenol 4,6-Dinitro-o-cresol 2-Chlorophenol 4-Chloro-3-methylphenol 4-Nitrophenol m-Cresol o-Cresol p-Cresol Pentachlorophenol Phenol
21	Extractables, Phenoxy Acid Herbicides	
22	Extractables, Organochlorine Pesticides	
23	Extractables, Neutral -Chlorinated	1,2,3,4-Tetrachlorobenzene 1,2,3,5-Tetrachlorobenzene 1,2,4,5-Tetrachlorobenzene 1,2,3-Trichlorobenzene 1,2,4-Trichlorobenzene 2,4,5-Trichlorotoluene Hexachlorobenzene Hexachlorobutadiene Hexachlorocyclopentadiene Hexachloroethane Octachlorostyrene Pentachlorobenzene

SCHEDULE 1 - ANALYTICAL TEST GROUP NUMBERS AND PARAMETERS

ANALYTICAL TEST GROUP #	NAME	PARAMETERS
24	Chlorinated Dibenzo-p-dioxins and Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin Octachlorodibenzo-p-dioxin Octachlorodibenzofuran Total heptachlorinated dibenzo-p-dioxins Total heptachlorinated dibenzofurans Total hexachlorinated dibenzo-p-dioxins Total hexachlorinated dibenzofurans Total pentachlorinated dibenzo-p-dioxins Total pentachlorinated dibenzofurans Total tetrachlorinated dibenzo-p-dioxins Total tetrachlorinated dibenzofurans
25	Solvent Extractables	Oil and grease
26	Fatty and Resin Acids	
27	Polychlorinated Biphenyls (PCBs) (Total)	PCBs (Total)

NOTE 1: Analyze for hexavalent chromium only if total chromium is greater than 1.0 milligrams per litre

NOTE 2: Analyze for alkyl leads only if total lead is greater than 1.0 milligrams per litre

NOTE 3 m-Xylene and p-Xylene often co-elute in the analysis A single combined result may be reported as m-Xylene

NOTE 4: Diphenylamine & N-Nitrosodiphenylamine often co-elute in the Gas Chromatography/Mass Spectrometry (GC/MS) analysis A single combined result may be reported as Diphenylamine

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTICAL TEST GROUP	LABORATORY SAMPLE CONTAINER	LABORATORY CONTAINER PRE-TREATMENT (ref. subsection 4(14))	TEST SPECIFIC SAMPLING PRECAUTIONS (ref. subsection 4(14))	MIN. SAM. VOL	PRESERVATION METHOD (ref. subsection 4(17))	STORAGE TIME (DAYS)
Chemical Oxygen Demand						
1	Sample containers and caps/liners must be composed only of one or more of the following materials: fluorocarbon resin, polyethylene terephthalate, glass, polystyrene, polypropylene, high or low density polyethylene. Metallic foil should not be used.	Generally no pre-treatment required for new containers.	If sample is high (>5%) in hydrocarbons or organic solvents, use glass or fluorocarbon resin sample container only.	25mL	i) None ii) Add sulphuric acid after sampling to lower pH to 2 but not <1.5	i) 4 ii) 28
Total Cyanide						
2	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	500mL	Add sodium hydroxide (NaOH) (cyanide free) to raise pH to 12.	7
Hydrogen Ion (pH)						
3	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	50mL	None	3
Nitrogen						
4a	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	100mL	See Analytical Test Group 1	i) 3 ii) 10
4b	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	50mL	None	5
Organic Carbon						
5a & b	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	100mL	See Analytical Test Group 1	i) 3 ii) 10

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTICAL TEST GROUP	LABORATORY SAMPLE CONTAINER	LABORATORY CONTAINER PRE-TREATMENT (ref. subsection 4(14))	TEST SPECIFIC SAMPLING PRECAUTIONS (ref. subsection 4(14))	MIN. SAM. VOL	PRESERVATION METHOD (ref. subsection 4(17))	STORAGE TIME (DAYS)
Total Phosphorus						
6	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	75mL	See Analytical Test Group 1	i) 14 ii) 28
Specific Conductance						
7	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	75mL	None	4
Suspended Solids						
8	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 1	500mL	None	7
Total Metals						
9	See Analytical Test Group 1	If pre-treatment necessary, soak overnight in a 5% solution of nitric acid (HNO3), followed by several rinses in distilled water.	See Analytical Test Group 1	100mL	Add nitric acid (HNO3) (containing <1mg/L of all analytes) to lower pH to <2.	30
Hydrides						
10	See Analytical Test Group 1	See Analytical Test Group 9	See Analytical Test Group 1	50mL	Either none or as for metals, if to be analyzed from same sample.	30
Chromium (Hexavalent)						
11	See Analytical Test Group 1	See Analytical Test Group 9	See Analytical Test Group 1	100mL	None	5

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1 ANALYTICAL TEST GROUP	Column 2 LABORATORY SAMPLE CONTAINER	Column 3 LABORATORY CONTAINER PRE-TREATMENT (ref. subsection 4(14))	Column 4 TEST SPECIFIC SAMPLING PRECAUTIONS (ref. subsection 4(14))	Col. 5 MIN. SAM. VOL.	Column 6 PRESERVATION METHOD (ref. subsection 4(17))	Column 7 STORAGE TIME (DAYS)
Mercury						
12	Glass or fluorocarbon resin with plastic lined cap.	See Analytical Test Group 9	No sample contact with metal except carbon steel or stainless steel.	200mL	Add 1-2mL nitric acid (HNO3) per 250mL sample followed by at least 0.5mL potassium dichromate (K2Cr2O7) solution to produce definite yellow colour.	7
Total Alkyl Lead						
13	See Analytical Test Group 1	See Analytical Test Group 9	Fill slowly to the top, no air space, avoid turbulence.	4L	None	4
Phenolics (4AAP)						
14	Glass or fluorocarbon resin with phenolic-free cap.	See Analytical Test Group 1	None	250mL	Precharge 250mL container with 1mL of solution containing 3N phosphoric acid (H3PO4) & 0.5g/L copper sulphate pentahydrate (CuSO4*5H2O) or add sulphuric acid solution prior to sampling to lower pH to 2 but not <1.5. Diluted acid may be used.	4
Sulphide						
15	See Analytical Test Group 1	See Analytical Test Group 1	See Analytical Test Group 13	250mL	Add 0.5mL 2N zinc acetate solution per 250mL sample followed dropwise by 5% sodium carbonate or 5% sodium hydroxide to pH 10.	7

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTICAL TEST GROUP	LABORATORY SAMPLE CONTAINER	LABORATORY CONTAINER PRE-TREATMENT (ref. subsection 4(14))	TEST SPECIFIC SAMPLING PRECAUTIONS (ref. subsection 4(14))	MIN. SAM. VOL	PRESERVATION METHOD (ref. subsection 4(17))	STORAGE TIME (DAYS)
Volatiles, 16	**Halogenated** Sample containers and caps/liners in contact with the sample to be analyzed must be composed of only one or more of the following materials: fluorocarbon resin, glass, metallic foil. (NOTE 1)	If pre-treatment necessary: Bottle: Sequence of extensive washing/hot water detergent, water, distilled water. Bake at 300°C for 8 h minimum. Cap: no pre-treatment.	Contact surfaces must be glass, fluorocarbon resin or stainless steel. See Analytical Test Group 13	25mL	Only for samples containing residual chlorine. Precharge bottles with 80mg sodium thiosulphate (Na2S2O3) per 1L. Keep in the dark.	7
Volatiles, 17	**Non-Halogenated** See Analytical Test Group 16	See Analytical Test Group 16	See Analytical Test Group 16	25mL	See Analytical Test Group 16	7
Volatiles, 18	**Water Soluble** See Analytical Test Group 16	See Analytical Test Group 16	See Analytical Test Group 16	25mL	See Analytical Test Group 16	7
Extractables, 19	**Base Neutral** Amber glass or fluorocarbon resin with fluorocarbon resin lined cap.	If pre-treatment necessary: Bottle: Sequence of extensive washing/hot water, detergent, water, distilled water Bake at 300°C for 8 h minimum or 3 rinses with pesticide grade or distilled in glass hexane and dichloromethane. Cap. no pre-treatment.	Contact surfaces must be glass, fluorocarbon resin or stainless steel.	800mL	None	30
Extractables, 20	**Acid (Phenolics)** See Analytical Test Group 19	See Analytical Test Group 19	See Analytical Test Group 19	800mL	None	30

SCHEDULE 2 - SAMPLING PRINCIPLES

Column 1	Column 2	Column 3	Column 4	Col. 5	Column 6	Column 7
ANALYTICAL TEST GROUP	LABORATORY SAMPLE CONTAINER	LABORATORY CONTAINER PRE-TREATMENT (ref. subsection 4(14))	TEST SPECIFIC SAMPLING PRECAUTIONS (ref. subsection 4(14))	MIN. SAM. VOL	PRESERVATION METHOD (ref. subsection 4(17))	STORAGE TIME (DAYS)
Extractables, Phenoxy Acid Herbicides						
21	See Analytical Test Group 19	See Analytical Test Group 19	See Analytical Test Group 19	800mL	None	30
Extractables, Organochlorine Pesticides						
22	Amber glass or fluorocarbon resin with foil or fluorocarbon resin lined cap. (NOTE 1)	See Analytical Test Group 19	See Analytical Test Group 19	800mL	None	30
Extractables, Neutral-Chlorinated						
23	See Analytical Test Group 22	See Analytical Test Group 19	See Analytical Test Group 19	800mL	None	30
Chlorinated Dibenzo-p-dioxins and Dibenzofurans						
24	See Analytical Test Group 19	See Analytical Test Group 19	See Analytical Test Group 19	1L	None	30
Solvent Extractables						
25	Clear glass or fluorocarbon resin with foil or fluorocarbon resin lined cap. (NOTE 1)	See Analytical Test Group 1	See Analytical Test Group 19	800mL	None	7
Fatty and Resin Acids						
26	See Analytical Test Group 22	See Analytical Test Group 19	See Analytical Test Group 19	800mL	None	30
Polychlorinated Biphenyls (PCBs)						
27	See Analytical Test Group 22	See Analytical Test Group 19	See Analytical Test Group 19	800mL	None	30

NOTE 1: Fluorocarbon resin lined caps should be used where sample pH is outside the neutral range.

SCHEDULE 3, PART A - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1 ANALYTICAL TEST GROUP #	Column 2 PARAMETERS CONVENTIONAL AND METAL PARAMETERS	Column 3 SAMPLE PREPARATION METHOD PRINCIPLES	Column 4 INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 5 ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 6 ANALYTICAL METHOD DETECTION LIMITS mg/L
1	Chemical oxygen demand (COD)	Preparation for measurement system as appropriate followed by reflux or oven digestion at 150°C in presence of oxidizing reagents	Back titration or Colourimetric measurement of trivalent chromium (Cr III)	N/A	10
2	Total cyanide	Acid distillation	Ion Chromatography or Colourimetry or Specific Ion Electrode or Titration	Polarography via the method of standard addition in the presence of suitable electrolyte	0.005
3	Hydrogen ion (pH)	Preparation for measurement system as appropriate	pH electrode and pH meter	N/A	N/A
4a	Ammonia plus Ammonium	Preparation for measurement system as appropriate eg distillation	Colourimetry or Specific Ion Electrode or Titration or Ion Chromatography	N/A	0.25 as Nitrogen
	Total Kjeldahl nitrogen	Preparation for measurement system as appropriate followed by Kjeldahl digestion procedure	Colourimetry or Specific Ion Electrode or Titration or Ion Chromatography	N/A	0.5 as Nitrogen
4b	Nitrate + Nitrite	Preparation for measurement system as appropriate	Colourimetry or Ion Chromatography	N/A	0.25 as Nitrogen

SCHEDULE 3, PART A - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS CONVENTIONAL AND METAL PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS mg/L
5a	Dissolved organic carbon (DOC)	Preparation for measurement system as appropriate followed by filtration through glass fibre filter, retention size approximately 2 micrometers	Quantitative conversion of carbon to carbon dioxide (CO2) by one of: i) Ultra violet persulphate digestion or ii) combustion at >800°C with a catalyst or iii) combustion at >1100°C, catalyst optional followed by infrared or colourimetric detection. DOC may be determined directly using a sample free of inorganic carbon or as the difference between total carbon and inorganic carbon.	N/A	0.5 as Carbon

SCHEDULE 3, PART A - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS CONVENTIONAL AND METAL PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS mg/L
5b	Total organic carbon (TOC)	Preparation for measurement system as appropriate. Particulates must be reduced in size sufficiently to ensure effective processing by the measurement system. Particulates may be separated from the liquid with subsequent exclusive analysis of both phases	Quantitative conversion of carbon to carbon dioxide (CO2) by one of: i) Ultra violet persulphate digestion or ii) combustion at >800°C with a catalyst or iii) combustion at >1100°C, catalyst optional followed by infrared or colourimetric detection. TOC may be determined directly using a sample free of inorganic carbon or as the difference between total carbon and inorganic carbon or by appropriate combination of the results from the analysis of the sample phases.	N/A	5 as Carbon
6	Total phosphorus	Preparation for measurement system as appropriate followed by perchloric acid digestion or a mixture of nitric acid to sulphuric acid (HNO3/H2SO4) at a ratio of 5:1 or a Kjeldahl equivalent mixture.	Colourimetry or Inductively Coupled Plasma - Atomic Emission Spectrometry	N/A	0.1 as Phosphorus

SCHEDULE 3, PART A - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1 ANALYTICAL TEST GROUP #	Column 2 PARAMETERS CONVENTIONAL AND METAL PARAMETERS	Column 3 SAMPLE PREPARATION METHOD PRINCIPLES	Column 4 INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 5 ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 6 ANALYTICAL METHOD DETECTION LIMITS mg/L
7	Specific conductance	Preparation for measurement system as appropriate	Conductivity meter and cell	N/A	5 µS/cm
8	Total suspended solids (TSS)	Preparation for measurement system as appropriate	Filtration - particle retention of glass fibre filter < or = 2 micrometres followed by drying of filter and particulates at 103°C ± 3°C and gravimetry	N/A	5
	Volatile Suspended solids (VSS)	Perform TSS analysis	Ignite filter at 550°C for 4 hr. or until filter weight remains constant.	N/A	10
9	Aluminum	Nitric evaporation or aqua regia digestion	Atomic absorption spectrometry and/or Emission Spectrometry - Inductively Coupled Plasma (ICP) or Direct Current Argon Plasma Spectrometry (DCP)	See Analytical Test Group 2	0.03
	Beryllium				0.01
	Cadmium				0.002
	Chromium				0.02
	Cobalt				0.02
	Copper				0.01
	Lead				0.03
	Molybdenum				0.02
	Nickel				0.02
	Silver				0.03
	Thallium				0.03
	Vanadium				0.03
	Zinc				0.01

SCHEDULE 3, PART A - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS CONVENTIONAL AND METAL PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS mg/L
10	Antimony Arsenic Selenium	Acid Digestion	Hydride Generation Atomic Absorption	See Analytical Test Group 2	0.005 0.005 0.005
11	Chromium (Hexavalent) (Analyze for hexavalent chromium only if total chromium >1.0mg/L)	I) None II) Solvent extraction	I) Colourimetry II) Atomic absorption	See Analytical Test Group 2	0.01
12	Mercury	Oxidative acid digestion	Cold vapour atomic absorption	N/A	0.0001
13	Tetra-alkyl lead Tri-alkyl lead (-inorganic ligand) (Analyze for alkyl leads only if total lead is >1.0mg/L)	I) Liquid/liquid extraction II) Derivatization	I) Colourimetry using Dithiozone reagent or Atomic absorption II) Gas Liquid Chromatography	N/A	0.002 0.002
14	Phenolics (4AAP)	Preparation for measurement system as appropriate followed by distillation from acidified (pH <4) sample	Colourimetry of buffered sample or Colourimetry of chloroform extract	N/A	0.002
15	Sulphide	Filtration and dissolution of precipitate	Methylene blue colourimetry or Specific Ion Electrode or Ion chromatography	See Analytical Test Group 2	0.02

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
16	1,1,2,2-Tetrachloroethane	Purge and trap	Gas Chromatography/ Mass Spectrometry (GC/MS) Capillary column	Gas Chromatography/ Electron Capture or Hal Single capillary column	10*
	1,1,2-Trichloroethane				10*
	1,1-Dichloroethane				10*
	1,1-Dichloroethylene				10*
	1,2-Dichlorobenzene				10*
	1,2-Dichloroethane (Ethylene dichloride)				10*
	1,2-Dichloropropane				10*
	1,3-Dichlorobenzene				10*
	1,4-Dichlorobenzene				10*
	Bromoform				10*
	Bromomethane				ND*
	Carbon tetrachloride				10*
	Chlorobenzene				10*
	Chloroform				10*
	Chloromethane				ND*
	Cis-1,3-Dichloropropylene				10*
	Dibromochloromethane				10*
	Ethylene dibromide				10*
	Methylene chloride				10*
	Tetrachloroethylene (Perchloroethylene)				10*
	Trans-1,2-Dichloroethylene				10*
	Trans-1,3-Dichloropropylene				ND*
	Trichloroethylene				10*
	Trichlorofluoromethane				10*
	Vinyl chloride (Chloroethylene)				ND*

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1 ANALYTICAL TEST GROUP #	Column 2 PARAMETERS ORGANIC PARAMETERS	Column 3 SAMPLE PREPARATION METHOD PRINCIPLES	Column 4 INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 5 ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 6 ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
17	Benzene	Purge and trap	Gas Chromatography/ Mass Spectometry (GC/MS) Capillary column	Gas Chromatography Flame Ionization or Photo Ionization Single capillary column	10*
	Ethylbenzene				10*
	Styrene				10*
	Toluene				10*
	o-Xylene				10*
	m-Xylene/p-Xylene (NOTE 1)				10*
18	Acrolein	Purge and trap	Gas Chromatography/ Mass Spectrometry (GC/MS) Capillary column	Gas Chromatography Electron Capture/Hall & Flame Ionization/ Photo Ionization Single capillary column	ND*
	Acrylonitrile				ND*

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1 ANALYTICAL TEST GROUP #	Column 2 PARAMETERS ORGANIC PARAMETERS	Column 3 SAMPLE PREPARATION METHOD PRINCIPLES	Column 4 INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 5 ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	Column 6 ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
19	Acenaphthene	Liquid/liquid extraction	Gas Chromatography/ Mass Spectrometry (GC/MS) Capillary column	High Performance Liquid Chromotography Ultra Violet or Fluorescence Detection	10*
	5-nitro Acenaphthene				10*
	Acenaphthylene				10*
	Anthracene				10*
	Benz(a)anthracene				10*
	Benzo(a)pyrene				10*
	Benzo(b)fluoranthene				10*
	Benzo(g,h,i)perylene				10*
	Benzo(k)fluoranthene				10*
	Camphene				10*
	1-Chloronaphthalene				10*
	2-Chloronaphthalene				10*
	Chrysene				10*
	Dibenz(a,h)anthracene				10*
	Fluoranthene				10*
	Fluorene				10*
	Indeno(1,2,3-cd)pyrene				10*
	Indole				ND*
	1-Methyl naphthalene				10*
	2-Methyl naphthalene				10*
	Naphthalene				10*
	Perylene				10*
	Phenanthrene				10*
	Pyrene				10*

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
19 cont'd	Benzylbutylphthalate	Liquid/liquid extraction	Gas Chromatography/ Mass Spectrometry (GC/MS) Capillary column	N/A	10*
	Bis(2-ethylhexyl)phthalate				10*
	Di-n-butylphthalate				10*
	4-Bromophenyl phenyl ether				10*
	4-Chlorophenyl phenyl ether				10*
	Bis(2-chloroisopropyl)ether				10*
	Bis(2-chloroethyl)ether				10*
	2,4-Dinitrotoluene				10*
	2,6-Dinitrotoluene				10*
	Bis(2-chloroethoxy)methane				10*
	Diphenylamine (NOTE 2)				10*
	N-Nitrosodiphenylamine (NOTE 2)				10*
	N-Nitrosodi-n-propylamine				10*

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
20	2,3,4,5-Tetrachlorophenol	Liquid/liquid extraction pH adjusted to <2 Derivaitzation, if appropriate Cleanup	Gas Chromatography/ Mass Spectrometry (GC/MS) Capillary column	N/A	10*
	2,3,4,6-Tetrachlorophenol				10*
	2,3,5,6-Tetrachlorophenol				10*
	2,3,4-Trichlorophenol				10*
	2,3,5-Trichlorophenol				10*
	2,4,5-Trichlorophenol				10*
	2,4,6-Trichlorophenol				10*
	2,4-Dimethylphenol				10*
	2,4-Dinitrophenol				10*
	2,4-Dichlorophenol				10*
	2,6-Dichlorophenol				10*
	4,6-Dinitro-o-cresol				10*
	2-Chlorophenol				10*
	4-Chloro-3-methylphenol				10*
	4-Nitrophenol				10*
	m-Cresol				10*
	o-Cresol				10*
	p-Cresol				10*
	Pentachlorophenol				10*
	Phenol				10*
21	Extractables, Phenoxy Acid Herbicides	N/A	N/A	N/A	N/A
22	Extractables, Organochlorine Pesticides	N/A	N/A	N/A	N/A

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
23	1,2,3,4-Tetrachlorobenzene	Liquid/liquid extraction Neutral pH Cleanup if necessary	Gas Liquid Chromatography Electron capture Dual capillary or Gas Chromatography/ Mass Spectroscopy (GC/MS) Capillary column	N/A	0.01
	1,2,3,5-Tetrachlorobenzene				0.01
	1,2,4,5-Tetrachlorobenzene				0.01
	1,2,3-Trichlorobenzene				0.01
	1,2,4-Trichlorobenzene				0.01
	2,4,5-Trichlorotoluene				0.01
	Hexachlorobenzene				0.01
	Hexachlorobutadiene				0.01
	Hexachlorocyclopentadiene				0.01
	Hexachloroethane				0.01
	Octachlorostyrene				0.01
	Pentachlorobenzene				0.01
24	2,3,7,8-Tetrachlorodibenzo-p-dioxin	Liquid/liquid extraction and cleanup or If TSS >15mg/L filter sample, extract solids by Soxhlet using toluene, extract filtrate normally, combine both extracts	Gas Chromatography/ Mass Spectroscopy (GC/MS) Capillary column	N/A	0.0003
	Octachlorodibenzo-p-dioxin				0.0003
	Octachlorodibenzofuran				0.0003
	Total heptachlorinated dibenzo-p-dioxins				0.0003
	Total heptachlorinated dibenzofurans				0.0003
	Total hexachlorinated dibenzo-p-dioxins				0.0003
	Total hexachlorinated dibenzofurans				0.0003
	Total pentachlorinated dibenzo-p-dioxins				0.0003
	Total pentachlorinated dibenzofurans				0.0003
	Total tetrachlorinated dibenzo-p-dioxins				0.0003
	Total tetrachlorinated dibenzofurans				0.0003

SCHEDULE 3, PART B - ANALYTICAL PRINCIPLES & ANALYTICAL METHOD DETECTION LIMITS

Column 1	Column 2	Column 3	Column 4	Column 5	Column 6
ANALYTICAL TEST GROUP #	PARAMETERS ORGANIC PARAMETERS	SAMPLE PREPARATION METHOD PRINCIPLES	INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ALTERNATE INSTRUMENTAL MEASUREMENT METHOD PRINCIPLES	ANALYTICAL METHOD DETECTION LIMITS FOR STANDARDS IN REAGENT WATER µg/L
25	Oil and Grease	Acidify with a mineral acid to approximately pH 2 Liquid/liquid extraction plus solvent rinsings of sample containers	Gravimetric	N/A	1000
26	Fatty & Resin Acids	N/A	N/A	N/A	N/A
27	Polychlorinated Biphenyls (PCBs) (Identify aroclors present & total concentration)	Liquid/liquid extraction Neutral pH Cleanup if necessary	Gas Liquid Chromatography Electron capture Single capillary column or Gas Chromatography/ Mass Spectroscopy (GC/MS) Capillary column Report as PCB Aroclors	N/A	0.1

NOTE 1: m-Xylene and p-Xylene often co-elute in the analysis. A single combined result may be reported as m-Xylene.

NOTE 2: Diphenylamine & N-Nitrosodiphenylamine often co-elute in the Gas Chromatography/Mass Spectrometry (GC/MS) analysis. A single combined result may be reported as Diphenylamine

* The Analytical Method Detection Limits (MDLs) shown for analytical test groups 16 - 20 inclusive are interim values. These values will be replaced with parameter specific MDLs by an amendment to the regulation by November 1, 1988. The MDLs will be determined from industry and MOE data generated using the MDL calculation procedure and will be as close to 1µg/L as possible.

EXPLANATORY NOTES TO ONTARIO REGULATION 358/88: EFFLUENT MONITORING - GENERAL

INTRODUCTION

These Explanatory Notes provide, where appropriate, an expanded description of each of the Sections in "Ontario Regulation 358/88: Effluent Monitoring - General" to further the reader's understanding.

The general regulation prescribes common monitoring and reporting requirements to be used in conjunction with the specific sectoral monitoring regulations.

GENERAL REGULATION SECTION 1: DEFINITIONS

This section of the regulation provides:

- clarification of terms used in the regulation having several possible interpretations;
- definitions for technical terms used in the regulation which may not be in common usage; and
- definitions for those terms which have a different meaning in the regulation than those found in a dictionary or through common use.

Although applying as well to each of the specific sectoral monitoring regulations, the definitions in the general regulation may be modified in any of the sectoral effluent monitoring regulations to suit specific needs.

The definition section does not re-define terms which are already defined in the Environmental Protection Act under which the regulation is written.

GENERAL REGULATION SECTION 2: PURPOSE AND APPLICATION

The purpose of this regulation is to prescribe common flow measurement, sampling, analysis, toxicity testing, recording, and reporting requirements for sectoral effluent monitoring regulations.

This regulation applies only in respect of monitoring obligations under a Sectoral Effluent Monitoring Regulation, and in the event of conflict between this regulation and a Sectoral Effluent Monitoring Regulation, the latter prevails.

GENERAL REGULATION SECTION 3: SAMPLING REQUIREMENTS

This section specifies the approved principles and protocols for sampling.

Schedule 2 provides the following information for the collection of samples to be analyzed for each of the analytical test groups (ATGs):

- types of laboratory sample containers;
- container pre-treatment;
- sampling precautions;
- minimum sample volumes;
- preservation methods;
- maximum storage times.

All samples must be placed without delay in an environment cooled to below 10 degrees Celsius but above the freezing point of the sample and stored within that temperature range until analyzed.

Process and Combined Effluent Sampling Points

Samples for all parameters, except sulfides (ATG 15) and volatiles (ATGs 16, 17, 18), must be taken by one of the following specified techniques:

- during the first 12 months of monitoring, samples from effluents with either variable or non-variable flow shall be collected by one of the four techniques listed in subsection 3(4) of the general regulation;
- within 3 months, after 12 months of monitoring, samples from process effluents with variable flow shall only be collected by either of the techniques listed in clause 3(4)(a) or 3(4)(b) of the general regulation;
- for sulfides (ATG 15) and volatiles (ATGs 16, 17, 18) 3 equal volume grab samples must be taken at intervals of at least 6 hours over a 24 hour period. These grab samples are to be combined in the laboratory immediately prior to analysis.

Section 3(11) requires that separate containers be used to collect composite samples for the analysis of cyanide (ATG 2), phenolics (ATG 14), and solvent extractables (ATG 25) with preservation chemicals being added prior to sampling for cyanide and phenolics.

Other Effluent Sampling Points

For once through cooling water sampling points, composite samples consisting of 3 equal volume grab samples must be taken at intervals of at least 6 hours over a 24 hour period and combined prior to analysis. Samples for the analysis of ATG 15 and ATGs 16-18 must be combined in the laboratory immediately prior to analysis, whereas all other samples may be combined in the field.

For stormwater, emergency overflow, and waste disposal site effluent sampling points, a single set of grab samples shall be collected.

For each of the sampling points where grab samples are permitted in the regulation, more accurate sampling methods - such as more frequent grab samples or composite sampling devices, as specified for process and combined effluent sampling points, may be substituted. However, samples for ATGs 15-18 must be grab samples.

General Cleanliness Requirements

It is the responsibility of the discharger to ensure that sample containers are clean and free of the analytes of interest and any interferences at the time of sampling.

Laboratory sample containers, ideally, should not be re-used. Contamination of samples may result from improperly cleaned sampling equipment or containers, causing false positives or artificially elevated results.

GENERAL REGULATION SECTION 4: ANALYTICAL REQUIREMENTS

Section 4 specifies the analytical requirements for all samples collected. Schedule 3 sets out, for each parameter in the analytical test groups, the following information:

- sample preparation method principles;
- instrumental measurement method principles;
- alternate instrumental measurement method principles;
- analytical method detection limits.

For analytical test groups 16 to 27, Schedule 3 specifies the method detection limits for standards in reagent water rather than in the "as found" effluent matrix.

The instrumental measurement method principles apply to the analysis of both routine monitoring and characterization samples but the alternate instrumental measurement method principles apply only to the analysis of routine monitoring samples.

In Schedule 3, the sample preparation method principle listed for several parameters states "preparation for measurement system as appropriate". The specific preparation required will be dependent upon the sample matrix to be analyzed. The Ministry recommends following good laboratory practice to determine the appropriate sample preparation which will effectively eliminate interferences.

Analytical method detection limits (MDLs) must be determined for each parameter following the procedure described in the Ontario Ministry of the Environment publication entitled "Estimation of Analytical Method Detection Limits (MDL)"(1), prior to the analysis of any samples.

The analytical method detection limits (MDLs) for analytical test groups 16-20 which appear in the general regulation are interim values only. Compound specific MDLs will be determined for the Volatiles and Extractables, Base Neutral and Acid (Phenolics) using industry and Ministry generated data through the procedure outlined in the Ontario Ministry of the Environment publication entitled "Estimation of Analytical Method Detection Limits (MDL)" (1). These MDLs will replace the interim values, listed in Schedule 3 part b, within 5 months of the date of promulgation of the Petroleum regulation (i.e., one month before the monitoring under the regulation takes effect). The compound specific MDLs will be as close to 1 part per billion (ppb) as possible, but will reflect the analytical variability associated with each parameter.

Samples collected for the analysis of the organic volatiles (ATGs 16, 17, 18) should be combined in a purge vessel in the laboratory immediately prior to analysis. Where the analytical equipment does not permit compositing in a purge vessel, the Ministry strongly discourages the compositing of volatile organic samples in refrigerated cold rooms. This practice is known to result in the contamination of samples with fluorocarbons originating from the cold room cooling system.

Section 4(4) specifies 6 calibration requirements for all analytical measurement systems.

Section 4(6) of the general regulation also requires analytical quality control samples. These are intended to demonstrate that analyses of the same substances performed by different analysts at different times and places are comparable within known statistical confidence limits.

The results of the analytical quality control samples are not to be reported to the Ministry routinely, but must be available for inspection upon request.

GENERAL REGULATION SECTION 5: TOXICITY TESTING

Section 5 specifies the following requirements for the fish toxicity and Daphnia magna acute lethality toxicity tests, including:

- volumes of collected samples;
- container materials;
- sample headspace minimization;
- maximum sample storage time;
- sample storage temperature;
- relevant MOE test protocols.

GENERAL REGULATION SECTION 6: FLOW MEASUREMENT

Section 6 specifies flow accuracy requirements for the different stream types together with the general requirements of proper installation, calibration, and maintenance of the flow measuring devices.

Flow accuracies are specified for continuous flow measurement devices as within plus or minus 5% of the actual flow for the primary device and within plus or minus 2% of the full-scale flow for the secondary flow measuring device.

Continuous flow measurement is required for all process effluents.

Flow measurement must be continuous for combined effluents and accurate on a daily basis to within plus or minus 20% of the actual flow.

Flow measurement at the time of sampling for other effluents must also be accurate to within plus or minus 20% of the actual flow.

GENERAL REGULATION SECTION 7: REPORTING

All information which is considered by the discharger to be confidential business information must be so identified on each page.

The reporting requirements under section 7 can be consolidated in two reports:

An **Initial Report** under section 7(1) with background information on the plant site and on the equipment and laboratories used to carry out the regulatory requirements.

A **Monitoring Report** covering:

- **analytical results**, under section 7(2), in written and electronic format, including on-line analyzer data, within a specified time period after analysis;
- **flow measurement data**, also in written and electronic format under section 7(4);

Initial Report

Each discharger must provide copies of the Initial Report to the Ministry's Regional Director before the start of the monitoring program. Dischargers are requested to provide four copies of the Initial Report, including attachments.

This information is required to provide background details on the industrial site in order to aid in the interpretation of monitoring results. It is intended that the Initial Report will document the discharger's intentions and procedures for complying with the regulation.

The report will also provide a basis for the Ministry to check on compliance with requirements through audit inspections.

The Initial Report is to contain the following information:

- "A plot plan of the plant..." showing:
    - property boundaries
    - scale and compass direction
    - Universal Transverse Mercator (UTM) coordinates to allow referencing of monitoring locations
    - processing areas
    - effluents, intakes, monitoring locations and outfalls
    - sample and flow monitoring point reference numbers (to be provided by the Ministry);

- "A simplified overview block diagram of the plant...";

  The block diagram may be in a schematic form since the intent is to show the processes and chemicals used in the processes as an aid to the Ministry's understanding of substances present or potentially present in the effluent of the plant site.

  Much of the information to be supplied with the block diagram may have been provided prior to regulation formulation; however, the information should be resubmitted within the regulation.

  The onus is on the discharger to identify the on-site substances known to be hazardous and likely to be released to a watercourse;

- "A list of the types and quantities of chemicals added to...cooling water...in the previous calendar year...";

  Information on substances such as algicides, anti-corrosives and disinfectants added to cooling water, will be helpful in determining the relative impact from this source;

- "A description of sampling devices... ";

  Self explanatory;

- "A description of any on-line analyzers...";

  Self explanatory;

- "A description of flow measurement methods and devices...and documentation of calibration...";

  The calibration report should identify the agency, contractor or supplier that carried out the calibration;

- "...maximum rated flow capacity for each flow measuring device...";

  Information on maximum rated flow capacity is required to aid in screening flow data for errors;

- "A description of rain-gauging devices...and methods...";

  Self explanatory;

- "...name and address of the laboratory...expected to carry out...test procedures.";

  Self explanatory;

- "A listing of sample preparation...method principles and...detection limits to be used in the laboratories.";

  A detailed questionnaire has been sent in advance to all commercial laboratories which will likely be analyzing MISA samples outlining this requirement.

The Ministry is preparing a guideline for preparation of the Initial Report to be available in July of 1988.

Monitoring Report

Analytical Results

The regulation requires submission of analytical results, including chemistry and toxicity data, to the Regional Director, care of the local District Office of the Ministry of the Environment. Both written and electronic forms of the data must be provided.

In order to facilitate the transfer of data, the Ministry has developed computer programs which provide for entry of the data and which produce the analytical results report in both hard-copy (paper) and electronic media (floppy diskettes), as described below:

- The MISA Data Entry System (MIDES) will be customized for each discharger by Ministry staff to include all data entry codes, sampling locations and monitoring parameters, for the different frequencies of sampling. The program will be provided free of charge to dischargers. The formats that the dischargers are required to use are defined in the Users Manual, which will be provided to each discharger;

- A separate program - The Toxicity Relational Database System (TOXDATA) - outlines the formats to be used when submitting results from fish toxicity and Daphnia magna toxicity tests. The TOXDATA system also provides a means for the discharger to manage the data. Both electronic and written formats are produced.

Both of the above programs will produce the transmittal sheet which must be signed by the direct discharger. The statement of transmittal on the sheet will be the following: "The information attached is submitted under Ontario Regulation 358/88."

The analytical results must be reported within the time frames specified in the regulation, as follows:

- within 30 days of the end of the month in which samples were collected for daily, thrice weekly, or weekly monitoring;
- within 60 days of the date the samples were collected for monthly or quarterly samples. The exceptions to this reporting requirement are dioxin and furan results (ATG 24). The Ministry recognizes that the turnaround time for these samples may be longer than 60 days. Therefore, reporting of dioxin and furan data has been included in the 90 day reporting requirement section;
- within 90 days of the date on which samples were collected for characterization purposes. Dioxin and furan samples have also been included in this reporting group.

Flow Measurement Data

Flow measurement information must accompany the routine analytical data report and must also be reported in electronic and written format within 30 days of the end of the month in which the flow was measured. The MIDES program described above will also accommodate the submission of these data.

ADDITIONAL NOTES

Routine Reporting of Intake Water Information

Dischargers are requested to inform the Ministry in their initial reports if it is their intention to routinely submit intake water data. This should include descriptions of locations, sampling techniques, parameters by frequency, flow measurement techniques, and the like. The Ministry will then use this information in customizing the data reporting formats.

In the past, dischargers have reported net concentrations to the Ministry of the Environment to account for the contamination of intake waters due to natural causes and upstream discharges. The Ministry, in the current regulations, requires the reporting of actual discharge concentrations. Intake concentrations may be reported by the discharger to aid in the interpretation of net contributions of contaminants from a particular location.

The Ministry of Environment Data Acceptance Procedure

The Ministry District Office will check the submitted information before entering it into the Ministry data bases.

Analytical results and flow data are expected to be checked and entered within 30 days. Errors, or omissions will be followed up with the discharger, and provisions made to resubmit the data.

ONTARIO REGULATION 359/88

under the Environmental Protection Act

EFFLUENT MONITORING - PETROLEUM REFINING SECTOR

OFFICE CONSOLIDATION

THIS EDITION IS PREPARED FOR PURPOSES OF CONVENIENCE ONLY, AND FOR ACCURATE REFERENCE RECOURSE SHOULD BE HAD TO THE OFFICIAL VOLUMES OR THE ONTARIO GAZETTE.

Definitions

1.-(1) In this Regulation;

"audit sample" means a set of samples collected by a provincial officer from a sampling point of a direct discharger;

"General Effluent Monitoring Regulation" means Ontario Regulation 358/88;

"landfarm leachate" means untreated waste disposal site effluent collected from a landfarm, landspreading site or soil biodegradation area;

"once-through cooling water sampling point" includes a point in a once-through cooling water effluent stream situated before the place of discharge to a surface watercourse and after the addition of boiler feedwater treatment effluent, cooling tower blowdown or clean surface runoff;

"process change" means any change in equipment, production process or treatment process;

"travelling blank sample" means a quality control sample of uncontaminated water that accompanies a set of sample containers from the laboratory to a sampling point and that is opened, preserved, resealed and returned to the laboratory with the set of samples for analysis;

"travelling spiked blank sample" means a quality control sample of uncontaminated water to which a certain recorded quantity of standard solution and appropriate preservative is added in the laboratory a maximum of twenty-four hours before accompanying a set of sample containers from the laboratory to a sampling point and back, unopened, to the laboratory for analysis with the set of samples.

(2) The definitions in section 1 of the General Effluent Monitoring Regulation apply to this Regulation.

Purpose

2. The purpose of this Regulation is to establish a data base on effluent quality in the petroleum refining sector that, along with other pertinent information, will be used in the development of effluent limits for that sector.

Application

3.-(1) This Regulation applies only with respect to the following refineries:

Refinery	Location	Owner as of the 1st of May, 1988
Sarnia Refinery	City of Sarnia	Esso Petroleum Canada, a division of Imperial Oil Limited
Clarkson Refinery	City of Mississauga	Petro-Canada Inc.
Trafalgar Refinery	Town of Oakville	Petro-Canada Inc.
Corunna Manufacturing Complex	Township of Moore	Petrosar Limited
Sarnia Manufacturing Centre	Township of Moore	Shell Canada Products Limited
Sarnia Refinery	City of Sarnia	Suncor Inc., Sunoco Division
Nanticoke Refinery	City of Nanticoke	Texaco Canada Inc.

(2) This Regulation is a Sectoral Effluent Monitoring Regulation within the meaning of the General Effluent Monitoring Regulation.

(3) The monitoring obligations, including the sampling, analysis, toxicity testing, flow measurement, recording and reporting obligations of this Regulation shall be carried out in accordance with the General Effluent Monitoring Regulation.

(4) An obligation on a person to do a thing under this Regulation is discharged if another person has done it.

Sampling Points

4.-(1) Each direct discharger shall establish the following sampling points:

1. An emergency overflow sampling point on each emergency overflow effluent stream.

2. A once-through cooling water sampling point on each once-through cooling water effluent stream.

3. A process effluent sampling point on each process effluent stream.

4. A storm water sampling point on each storm water effluent stream.

(2) The sampling points established under subsection (1) shall be used for all sampling required by this Regulation, except that a direct discharger may use alternate sampling points where that is acceptable to the Director.

Characterization

5.-(1) Each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (3) from each process effluent sampling point of that discharger,

(a) once within three months after the collection of the first sample under section 6;

(b) once not sooner than four months but not later than seven months after the collection of samples under clause (a);

(c) once in 1991 and in every third year thereafter; and

(d) once within thirty days after every process change that is expected to adversely affect the quality of that effluent.

(2) Clause (1)(d) does not apply to experimental process changes of less than thirty days in duration.

(3) Each direct discharger shall analyze each set of samples collected under subsection (1) for the parameters in Column 2 of Schedule A marked with an "X" in Column 7 of Schedule A.

Routine Monitoring - Daily

6.-(1) During each operating day, each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (3) from each process effluent sampling point of that discharger.

(2) Subsection (1) does not apply in respect of any day in which a sufficient volume of sample cannot be collected because of the collection of audit samples.

(3) Each direct discharger shall analyze each set of samples collected under subsection (1) for the parameters in Column 2 of Schedule A marked with an "X" in Column 4 of Schedule A.

Routine Monitoring - Three Times Weekly

7.-(1) On at least three separate operating days in each week, each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (2) from each process effluent sampling point of that discharger.

(2) Each direct discharger shall analyze each set of samples collected under subsection (1) for,

(a) the parameters in Column 2 of Schedule A marked with an "X" in Column 5 of Schedule A; and

(b) where chromium or zinc are used in the treatment of cooling water by that discharger, the parameters in Column 2 of Schedule A marked with a "Y" in Column 5 of Schedule A.

Routine Monitoring - Quarterly

8.-(1) On at least three separate operating days in one week in each quarter, each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (3) from each process effluent sampling point of that discharger.

(2) For the purposes of subsection (1), samples collected after the first sample collected under subsection (1) shall be collected no sooner than six weeks and no later than four months after the previous sampling.

(3) Each direct discharger shall analyze each set of samples collected under subsection (1) for the parameters in Column 2 of Schedule A marked with an "X" in Column 6 of Schedule A.

Routine Monitoring - Once-Through Cooling Water

9.-(1) On at least one operating day in each month, each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (2) from each once-through cooling water sampling point of that discharger.

(2) Each direct discharger shall analyze each set of samples collected under subsection (1) for,

- (a) the parameters in Column 2 of Schedule A marked with an "X" in Column 8 of Schedule A; and
- (b) where chromium or zinc are used in the treatment of cooling water by that discharger, the parameters in Column 2 of Schedule A marked with a "Y" in Column 8 of Schedule A.

Routine Monitoring - Storm Water

10.-(1) Before or during each discharge of storm water, each direct discharger shall collect a set of samples representative of that discharge and sufficient to perform all of the analyses required by subsection (2) from each storm water sampling point on each affected storm water effluent stream of that discharger.

(2) Each direct discharger shall analyze each set of samples collected under subsection (1) for the parameters in Column 2 of Schedule A marked with an "X" in Column 5 of Schedule A.

Routine Monitoring - Emergency Overflow

11.-(1) During each emergency overflow, each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (3) from each emergency overflow sampling point on each affected emergency overflow effluent stream of that discharger.

(2) Subsection (1) does not apply if the collection of samples would result in extraordinary danger to health or safety.

(3) Each direct discharger shall analyze each set of samples collected under subsection (1) for the parameters in Column 2 of Schedule A marked with an "X" in Column 5 of Schedule A.

Routine Monitoring - Landfarm Leachate

12.-(1) At least once in each year, each direct discharger shall collect a set of samples sufficient to perform all of the analyses required by subsection (2) from a discharge of landfarm leachate from that discharger's plant to a surface watercourse.

(2) Each direct discharger shall analyze the samples collected under subsection (1) for the parameters in Column 2 of Schedule A marked with an "X" in Column 6 of Schedule A.

(3) At least once during each discharge of landfarm leachate from the plant of a direct discharger to a surface watercourse, the direct discharger shall collect a set of samples from the discharge sufficient to perform all of the analyses required by subsection (4).

(4) Each direct discharger shall analyze the samples collected under subsection (3) for the parameters in Column 2 of Schedule A marked with an "X" in Column 5 of Schedule A.

Quality Control Samples

13.-(1) For the purposes of this section, "quality control samples" means,

(a) one duplicate sample for each sample collected under sections 6 to 8 for analysis for parameters in each analytical test group in Column 2 of Schedule A;

(b) one travelling blank sample for each sample collected under sections 6 to 8 for analysis for parameters in each analytical test group in Column 2 of Schedule A, except groups 1, 3 and 8; and

(c) one travelling spiked blank sample for each sample collected under sections 6 to 8 for analysis for parameters in analytical test groups 16 to 24, 26 and 27 in Column 2 of Schedule A.

(2) Each travelling spiked blank sample required to be analyzed by this section shall be prepared with a standard solution containing at least the parameters to be analyzed for.

(3) Each direct discharger shall collect quality control samples from one process effluent sampling point of that discharger once in each month concurrent with the sampling required by section 6 and shall analyze the samples for the parameters in Column 2 of Schedule A which are marked with an "X" in Column 4 of Schedule A.

(4) Each direct discharger shall collect quality control samples from one process effluent sampling point of that discharger once in each month concurrent with the sampling required by section 7 and shall analyze the samples for the parameters in Column 2 of Schedule A marked with an "X" or a "Y" in Column 5 of Schedule A and not marked with an "X" in Column 4 of Schedule A.

(5) Each direct discharger shall collect quality control samples from one process effluent sampling point of that discharger once in each quarter concurrent with the sampling required by section 8 and shall analyze the samples for the parameters in Column 2 of Schedule A marked with an "X" in Column 6 of Schedule A and not marked with an "X" in Column 4 or 5 of Schedule A.

Quality Control - Analytical Runs

14.-(1) With respect to analysis required under this Regulation, where there are consistently less than fourteen samples in each analytical run, the quality control samples referred to in subsection 4(6) of the General Effluent Monitoring Regulation may be processed once before the analysis of any samples and once after the processing of every fourteen samples in consecutive analytical runs, instead of at the times specified in that subsection.

(2) Each set of quality control samples referred to in subsection (1) shall be analyzed together in one analytical run.

Toxicity Testing

15.-(1) Each direct discharger shall collect a sample from each process effluent sampling point of that discharger once in each month on the same day as one of the sets of samples required by section 7 is collected, and shall perform a fish toxicity test on each of the samples required by this subsection.

(2) If the tests performed under subsection (1) in three consecutive months result in mortality for no more than two out of ten fish at all effluent concentrations, a direct discharger may thereafter collect the samples and perform the tests required by subsection (1) only once in each quarter, on the same day as one of the sets of samples required by section 8 is collected.

(3) Subsection (2) ceases to apply in the event that a test performed under it results in mortality for more than two out of ten fish at any effluent concentration.

(4) Once in each month on the same day as one of the sets of samples required by section 7 is collected, each direct discharger shall collect a sample from each process effluent sampling point of that discharger and shall perform thereon a *Daphnia magna* acute lethality toxicity test.

(5) In a month in which a sample is required to be collected for a fish toxicity test, the sample required by subsection (4) shall be collected together in the same container or set of containers with the fish toxicity test sample.

(6) Each direct discharger shall collect a sample from each once-through cooling water sampling point of that discharger once in each quarter on the same day as one of the sets of samples required by section 9 is collected and shall perform, on each of the samples required by this subsection,

(a) a fish toxicity test; and

(b) a Daphnia magna acute lethality toxicity test.

(7) A test performed in accordance with the procedures set out in Schedule VII of the Petroleum Refinery Liquid Effluent Guidelines, The Canada Gazette Part I, November 3, 1973, pg. 3547, satisfies the requirements of clause (6)(a).

Flow Measurement

16.-(1) Each direct discharger shall continuously measure the flow of each process effluent stream of that discharger at a location or set of locations representative of the flow at the sampling point established for that stream, and shall record the measured flow.

(2) Where the flow of a process effluent stream cannot be continuously measured on any day because of equipment malfunction and all reasonable care has been taken to avoid and correct the malfunction, the direct discharger may fulfil the requirement of subsection (1) by estimating the total daily flow of the stream and recording that estimate.

(3) Each direct discharger shall, at the time of each sampling, measure or estimate the flow of each once-through cooling water effluent stream, storm water effluent stream and emergency overflow effluent stream of that discharger at a location or set of locations representative of the flow at the sampling point established for that stream, and shall record the measured or estimated flow.

(4) Each direct discharger shall measure or estimate the flow of each discharge of landfarm leachate from the discharger's plant.

Reporting

17.-(1) Within seven days after this subsection comes into force, each direct discharger shall submit an initial report to the Director in respect of that direct discharger's plant.

(2) Each direct discharger shall report any changes to the information submitted under subsection (1) to the Director within thirty days after the end of the month during which the change occurs.

(3) Each direct discharger shall report to the Director the results of all analyses performed by or on behalf of the direct discharger under sections 5 to 15, including all positive numerical values at or above the analytical method detection limits calculated by the laboratory performing the analysis.

(4) Each direct discharger shall report to the Director the flow measurement information recorded in respect of each process effluent stream and once-through cooling water effluent stream of that discharger.

(5) Each direct discharger shall report to the Director the date and duration of each storm event, the amount of rainfall during that event and the date, duration and volume of each discharge of storm water to a surface watercourse.

(6) Each direct discharger shall report to the Director the date, duration and volume of each discharge of landfarm leachate to a surface watercourse.

(7) Each direct discharger shall report to the Director the date, location, duration and approximate volume of effluent discharged during each emergency overflow.

(8) The reports referred to in subsections (4) to (7) shall be submitted to the Director in writing within thirty days after the end of the month in which the information was recorded.

(9) At least thirty days before the collection of the first sample in each month, each direct discharger shall submit to the Director a schedule of sampling dates and times by location for all monthly, quarterly and characterization sampling in that month.

(10) Once in each quarter, each direct discharger shall submit a report to the Director summarizing the quantities of chemicals added to once-through cooling water, and stating the dates on which these additions occurred.

(11) Each direct discharger shall submit a report to the Director describing the variation in daily flow for a period of six months for each process effluent stream from which samples are collected other than by means of an automatic flow proportional composite sampling device, no later than one year after this section comes into force.

(12) The report referred to in subsection (11) shall include the raw data and calculation methods used to produce the report.

(13) Each direct discharger shall keep records of all sampling required by this Regulation, including, for each sample, the date and time of collection, sampling procedures used, the amount of sample dilution by preservative if dilution exceeds one per cent, and any incident likely to affect an analytical result.

(14) Each direct discharger shall develop a maintenance and calibration schedule for all sampling equipment and shall record the results of all maintenance and calibration performed.

(15) Records of all analytical methods used shall be kept by the direct discharger.

(16) Each direct discharger shall submit a report to the Director detailing the date, duration and cause of each sampling, toxicity testing, analytical and flow measurement malfunction or other problem, and remedial action taken, within thirty days after the end of the month in which the malfunction or problem occurs.

(17) All records and reports required to be kept or made by this Regulation shall be retained by the direct discharger for a period of two years.

Timing

18.-(1) This Regulation, except subsection 17(1), comes into force on the 1st day of December, 1988.

(2) Subsection 17(1) comes into force on the 1st day of September, 1988.

(3) Sections 7 to 12 and section 15 are revoked on the 1st day of December, 1989.

COLUMN DESCRIPTIONS FOR SCHEDULE A

Column 3:
- CAS #s = Chemical Abstract Series Numbers

Column 4:
- daily for process effluents only

Column 5:
- 3 times per week for process effluents
- during discharge for storm water, emergency overflows and landfarm leachate

Column 6:
- 3 daily samples within one week, each quarter for process effluent
- once per year for landfarm leachate

Column 7:
- all parameters to be analyzed in characterization samples

Column 8:
- once per month for once-through cooling water

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP #	NAME	PARAMETERS	CAS #s †					
27	Polychlorinated Biphenyls (PCBs) (Total)	PCBs (Total)	Unavailable				X	

† CAS #s - Chemical Abstract Series Numbers

* N/A - Not Applicable

** 4AAP - 4-amino antipyrine method

NOTE 1: Total organic carbon is to be analyzed three times per week only if the total suspended solids concentration exceeds 15 milligrams per litre.

NOTE 2: Analyze for hexavalent chromium only if total chromium is greater than 1.0 milligrams per litre.

NOTE 3: Analyze for alkyl leads only if total lead is greater than 1.0 milligrams per litre.

NOTE 4: m-Xylene and p-Xylene often co-elute in the analysis. A single combined result may be reported as m-Xylene.

NOTE 5: Diphenylamine & N-Nitrosodiphenylamine often co-elute in the Gas Chromatography/Mass Spectrometry (GC/MS) analysis. A single combined result may be reported as Diphenylamine.

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP #	NAME	PARAMETERS	CAS #s †					
1	Chemical Oxygen Demand	Chemical oxygen demand (COD)	N/A*			X	X	
2	Total cyanide	Total cyanide	57-12-5			X	X	
3	Hydrogen Ion (pH)	Hydrogen Ion (pH)	N/A*	X	X	X	X	X
4a	Nitrogen	Ammonia plus Ammonium	N/A*		X	X	X	
		Total Kjeldahl nitrogen	N/A*			X	X	
4b		Nitrate + Nitrite	N/A*			X	X	
5a	Organic carbon	Dissolved organic carbon (DOC)	N/A*		X	X	X	X
5b		Total organic carbon (TOC) (NOTE 1)	N/A*		X	X	X	X
6	Total phosphorus	Total phosphorus	N/A*		X	X	X	
7	Specific conductance	Specific conductance	N/A*			X	X	
8	Suspended solids	Total suspended solids (TSS)	N/A*		X	X	X	X
		Volatile suspended solids (VSS)	N/A*	X	X	X	X	X

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP #	NAME	PARAMETERS	CAS #s †					
9	Total metals	Aluminum	7429-90-5			X	X	
		Beryllium	7440-41-7			X	X	
		Cadmium	7440-43-9			X	X	
		Chromium	7440-47-3		Y	X	X	Y
		Cobalt	7440-48-4			X	X	
		Copper	7440-50-8			X	X	
		Lead	7439-92-1			X	X	
		Molybdenum	7439-98-7			X	X	
		Nickel	7440-02-0			X	X	
		Silver	7440-22-4			X	X	
		Thallium	7440-28-0			X	X	
		Vanadium	7440-62-2			X	X	
		Zinc	7440-66-6		Y	X	X	Y
10	Hydrides	Antimony	7440-36-0			X	X	
		Arsenic	7440-38-2			X	X	
		Selenium	7782-49-2			X	X	
11	Chromium (Hexavalent)	Chromium (Hexavalent) (NOTE 2)	7440-47-3			X	X	
12	Mercury	Mercury	7439-97-6			X	X	
13	Total alkyl lead	Tetra-alkyl lead (NOTE 3)	N/A*			X	X	
		Tri-alkyl lead (NOTE 3)	N/A*			X	X	
14	Phenolics (4AAP**)	Phenolics (4AAP**)	N/A*	X	X	X	X	X
15	Sulphide	Sulphide	N/A*		X	X	X	X

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

COLUMN 1		COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP #	NAME	PARAMETERS	CAS #s †					
16	Volatiles, Halogenated	1,1,2,2-Tetrachloroethane	79-34-5			X	X	
		1,1,2-Trichloroethane	79-00-5			X	X	
		1,1-Dichloroethane	75-34-3			X	X	
		1,1-Dichloroethylene	75-35-4			X	X	
		1,2-Dichlorobenzene	95-50-1			X	X	
		1,2-Dichloroethane (Ethylene dichloride)	107-06-2			X	X	
		1,2-Dichloropropane	78-87-5			X	X	
		1,3-Dichlorobenzene	541-73-1			X	X	
		1,4-Dichlorobenzene	106-46-7			X	X	
		Bromoform	75-25-2			X	X	
		Bromomethane	74-83-9			X	X	
		Carbon tetrachloride	56-23-5			X	X	
		Chlorobenzene	108-90-7			X	X	
		Chloroform	67-66-3			X	X	
		Chloromethane	74-87-3			X	X	
		Cis-1,3-Dichloropropylene	10061-01-5			X	X	
		Dibromochloromethane	124-48-1			X	X	
		Ethylene dibromide	106-93-4			X	X	
		Methylene chloride	75-09-2			X	X	
		Tetrachloroethylene (Perchloroethylene)	127-18-4			X	X	
		Trans-1,2-Dichloroethylene	156-60-5			X	X	
		Trans-1,3-Dichloropropylene	10061-02-6			X	X	
		Trichloroethylene	79-01-6			X	X	
		Trichlorofluoromethane	75-69-4			X	X	
		Vinyl chloride (Chloroethylene)	75-01-4			X	X	

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP \#	NAME	PARAMETERS	CAS #s †					
17	Volatiles, Non-Halogenated	Benzene	71-43-2		X	X	X	X
		Ethylbenzene	100-41-4		X	X	X	X
		Styrene	100-42-5			X	X	
		Toluene	108-88-3		X	X	X	X
		o-Xylene	95-47-6		X	X	X	X
		m-Xylene and p-Xylene (NOTE 4)	108-38-3		X	X	X	X
			& 106-42-3					
18	Volatiles, Water Soluble	Acrolein	107-02-8			X	X	
		Acrylonitrile	107-13-1			X	X	

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP #	NAME	PARAMETERS	CAS #s †					
19	Extractables, Base Neutral	Acenaphthene	83-32-9			X	X	
		5-nitro Acenaphthene	602-87-9			X	X	
		Acenaphthylene	208-96-8			X	X	
		Anthracene	120-12-7			X	X	
		Benz(a)anthracene	56-55-3			X	X	
		Benzo(a)pyrene	50-32-8			X	X	
		Benzo(b)fluoranthene	205-99-2			X	X	
		Benzo(g,h,l)perylene	191-24-2			X	X	
		Benzo(k)fluoranthene	207-08-9			X	X	
		Camphene	79-92-5			X	X	
		1-Chloronaphthalene	90-13-1			X	X	
		2-Chloronaphthalene	91-58-7			X	X	
		Chrysene	218-01-9			X	X	
		Dibenz(a,h)anthracene	53-70-3			X	X	
		Fluoranthene	206-44-0			X	X	
		Fluorene	86-73-7			X	X	
		Indeno(1,2,3-cd)pyrene	193-39-5			X	X	
		Indole	120-72-9			X	X	
		1-Methylnaphthalene	90-12-0			X	X	
		2-Methylnaphthalene	91-57-6			X	X	
		Naphthalene	91-20-3			X	X	
		Perylene	198-55-0			X	X	
		Phenanthrene	85-01-8			X	X	
		Pyrene	129-00-0			X	X	

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
#	ANALYTICAL TEST GROUP NAME	PARAMETERS	CAS #s †					
19	Extractables, Base Neutral (continued)	Benzylbutylphthalate	85-68-7				X	
		Bis(2-ethylhexyl)phthalate	117-81-7				X	
		Di-n-butylphthalate	84-74-2				X	
		4-Bromophenyl phenyl ether	101-55-3				X	
		4-Chlorophenyl phenyl ether	7005-72-3				X	
		Bis(2-chloroisopropyl)ether	108-60-1				X	
		Bis(2-chloroethyl)ether	111-44-4				X	
		2,4-Dinitrotoluene	121-14-2				X	
		2,6-Dinitrotoluene	606-20-2				X	
		Bis(2-chloroethoxy)methane	111-91-1				X	
		Diphenylamine (NOTE 5)	122-39-4				X	
		N-Nitrosodiphenylamine (NOTE 5)	86-30-6				X	
		N-Nitrosodi-n-propylamine	621-64-7				X	

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
#	ANALYTICAL TEST GROUP NAME	PARAMETERS	CAS #s †					
20	**Extractables**, Acid (Phenolics)	2,3,4,5-Tetrachlorophenol	4901-51-3			X	X	
		2,3,4,6-Tetrachlorophenol	58-90-2			X	X	
		2,3,5,6-Tetrachlorophenol	935-95-5			X	X	
		2,3,4-Trichlorophenol	15950-66-0			X	X	
		2,3,5-Trichlorophenol	933-78-8			X	X	
		2,4,5-Trichlorophenol	95-95-4			X	X	
		2,4,6-Trichlorophenol	88-06-2			X	X	
		2,4-Dimethylphenol	105-67-9			X	X	
		2,4-Dinitrophenol	51-28-5			X	X	
		2,4-Dichlorophenol	120-83-2			X	X	
		2,6-Dichlorophenol	87-65-0			X	X	
		4,6-Dinitro-o-cresol	534-52-1			X	X	
		2-Chlorophenol	95-57-8			X	X	
		4-Chloro-3-methylphenol	59-50-7			X	X	
		4-Nitrophenol	100-02-7			X	X	
		m-Cresol	108-39-4			X	X	
		o-Cresol	95-48-7			X	X	
		p-Cresol	108-44-5			X	X	
		Pentachlorophenol	87-86-5			X	X	
		Phenol	108-95-2			X	X	
21	**Extractables, Phenoxy Acid Herbicides**	This group does not apply to the Petroleum Refining Sector	Unavailable					
22	**Extractables, Organochlorine Pesticides**	This group does not apply to the Petroleum Refining Sector	Unavailable					

SCHEDULE A - MONITORING PARAMETERS AND FREQUENCIES

	COLUMN 1	COLUMN 2	COLUMN 3	COLUMN 4	COLUMN 5	COLUMN 6	COLUMN 7	COLUMN 8
ANALYTICAL TEST GROUP #	NAME	PARAMETERS	CAS #s †					
23	Extractables, Neutral -Chlorinated	1,2,3,4-Tetrachlorobenzene	634-66-2				X	
		1,2,3,5-Tetrachlorobenzene	634-90-2				X	
		1,2,4,5-Tetrachlorobenzene	95-94-3				X	
		1,2,3-Trichlorobenzene	87-61-6				X	
		1,2,4-Trichlorobenzene	120-82-1				X	
		2,4,5-Trichlorotoluene	6639-30-1				X	
		Hexachlorobenzene	118-74-1				X	
		Hexachlorobutadiene	87-68-3				X	
		Hexachlorocyclopentadiene	77-47-4				X	
		Hexachloroethane	67-72-1				X	
		Octachlorostyrene	29082-74-4				X	
		Pentachlorobenzene	608-93-5				X	
24	Chlorinated Dibenzo-p-dioxins and Dibenzofurans	2,3,7,8-Tetrachlorodibenzo-p-dioxin	1746-01-6				X	
		Octachlorodibenzo-p-dioxin	326-88-7				X	
		Octachlorodibenzofuran	Unavailable				X	
		Total heptachlorinated dibenzo-p-dioxins	Unavailable				X	
		Total heptachlorinated dibenzofurans	Unavailable				X	
		Total hexachlorinated dibenzo-p-dioxins	34465-46-8				X	
		Total hexachlorinated dibenzofurans	Unavailable				X	
		Total pentachlorinated dibenzo-p-dioxins	Unavailable				X	
		Total pentachlorinated dibenzofurans	Unavailable				X	
		Total tetrachlorinated dibenzo-p-dioxins	Unavailable				X	
		Total tetrachlorinated dibenzofurans	Unavailable				X	
25	Solvent Extractables	Oil and grease			X	X	X	X
26	Fatty and Resin Acids	This group does not apply to the Petroleum Refining Sector						

EXPLANATORY NOTES TO ONTARIO REGULATION 359/88: EFFLUENT MONITORING - PETROLEUM REFINING SECTOR

INTRODUCTION

These Explanatory Notes provide, where appropriate, an expanded description of each of the Sections in Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector to further the reader's understanding.

Using the methods established in the Effluent Monitoring - General Regulation, the Petroleum regulation specifies "when", "where" and "what" to sample and analyze in order to establish a data base on effluent quality for the Petroleum Refining Sector.

PETROLEUM REGULATION SECTION 1: DEFINITIONS

This section of the regulation provides:

- clarification of terms used in the regulation having several possible interpretations;
- definitions for technical terms used in the regulation which may not be in common usage;
- definitions for those terms which have a different meaning in the regulation than those found in a dictionary or through common use.

It is important to note that Section 1(2) states that the definitions in Section 1 of the general regulation also apply to this regulation.

The definition section does not re-define terms which are already defined in the Environmental Protection Act under which the regulation is written.

PETROLEUM REGULATION SECTION 2: PURPOSE

The purpose of this regulation is to establish a data base on effluent quality for the petroleum refining sector which, along with other pertinent information, will be applied to the development of effluent limits for that sector.

PETROLEUM REGULATION SECTION 3: APPLICATION

Section 3 lists the petroleum refineries to which this regulation applies and establishes, in Section 3(4), the general principle that each listed discharger is responsible for carrying out all of the requirements of this regulation.

Section 3(3) links this regulation with the general regulation by stating that sampling, analytical, toxicity testing, flow measurement, and reporting requirements specified in this regulation, must also be carried out in accordance with the provisions of the general regulation.

PETROLEUM REGULATION SECTION 4: SAMPLING POINTS

Section 4(1) specifies the requirement within Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector that sampling locations must be established on emergency overflow, cooling water, process effluent, and stormwater effluent streams, and that the sampling locations established under 4(1) be used so long as the regulation is in effect, unless alternate sampling locations are deemed acceptable by the Regional Director of the Ministry of the Environment.

PETROLEUM REGULATION SECTION 5: CHARACTERIZATION

The "how to" protocols for sampling and analysis, set out in Section 3 (Schedule 2) and Section 4 (Schedule 3) respectively, of the general regulation, also apply to this section.

Characterization requirements for petroleum refinery process effluents are set out in Section 5 and Column 7 of Schedule A of Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector.

Characterization is required initially (i.e. within 3 months of the first routine sampling), once between 4 and 7 months later, every 3 years thereafter, and within 30 days after each process change which could adversely affect effluent quality.

Characterization of refinery process effluents is not required after experimental process changes of less than 30 days duration.

PETROLEUM REGULATION SECTIONS 6, 7, 8, 9, 10, 11, AND 12: ROUTINE MONITORING

The "how to" protocols for sampling and analysis, set out in Section 4 (Schedule 2) and Section 5 (Schedule 3) respectively, of the general regulation, also apply to this section.

The requirements for routine chemical monitoring are set out in Sections 6, 7, 8, 9, 10, 11, and 12, and Schedule A of Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector for all frequencies of sampling.

Process Effluents

Process effluent streams are to be monitored at a point following final treatment, but prior to dilution.

Daily

Section 6 and Column 4 of Schedule A require direct dischargers to monitor for the following analytical test groups (ATG's):

- 3 (pH)
- 8b (volatile suspended solids)
- 14 (phenolics 4AAP).

Thrice Weekly

Section 7 and Column 5 of Schedule A require direct dischargers to monitor for the following analytical test groups (ATG's):

- 3 (pH)
- 4a (ammonia/ammonium nitrogen)
- 5a (dissolved organic carbon DOC)
- 5b (total organic carbon TOC - only if the TSS concentration exceeds 15 mg/L)
- 6 (total phosphorus)
- 8a (total suspended solids TSS)
- 8b (volatile suspended solids VSS)
- 14 (phenolics 4AAP)
- 15 (sulfide)
- 17 (volatiles, non-halogenated, except styrene)
- 25 (oil and grease)
- 9 (chromium and zinc only when used in the treatment of cooling water)

Quarterly

Section 8 and Column 6 of Schedule A require direct dischargers to monitor, in clusters of 3 daily samples taken within one week in each quarter, for all of the analytical test groups shown in column 2 of Schedule A with the following exceptions:

- 19 (extractables, base neutral except PAHs which are monitored)
- 23 (extractables, neutral chlorinated)
- 24 (dibenzo-p-dioxins/dibenzofurans)

Other Effluents

Section 9 and Column 8 of Schedule A require direct dischargers to monitor once-through cooling water, once per month for the following analytical test groups:

- 3 (pH)
- 5a (DOC)
- 5b (TOC - only if the TSS concentration exceeds 15 mg/l)
- 8a (TSS)
- 8b (VSS)
- 14 (phenolics 4AAP)
- 15 (sulfide)
- 17 (volatiles, non-halogenated, except styrene)
- 25 (oil and grease)
- 9 (chromium and zinc, only when used in the treatment of cooling water)

Sections 10 and 11 and Column 5 of Schedule A require dischargers to monitor storm water and emergency overflows when discharged to a surface watercourse for the following analytical test groups:

- 3 (pH)
- 4a (ammonium/ammonia nitrogen)
- 5a (DOC)
- 5b (TOC - only if the TSS concentration exceeds 15 mg/l)
- 6 (total phosphorus)
- 8a (TSS)
- 8b (VSS)
- 14 (phenolics 4AAP)
- 15 (sulfide)
- 17 (volatiles, non-halogenated, except styrene)
- 25 (oil and grease)

The samples must be collected near the beginning of each discharge period.

Each planned direct discharge to a receiving watercourse of landfarm leachate (which does not receive treatment), is to be monitored as set out in Section 12 and Column 5 of Schedule A for the thrice weekly list including chromium and zinc.
At least once per year, direct leachate discharges must also be monitored for the quarterly list, as set out in Section 12 and Column 6 of Schedule A.

PETROLEUM REGULATION SECTIONS 13 AND 14: QUALITY CONTROL

Section 13 specifies quality control samples to be collected monthly and quarterly from a process effluent sampling point to provide duplicate, travelling blank, and travelling spiked blank samples.

The monthly quality control sample is to be analyzed for the parameters set out in Column 5 of Schedule A for the thrice weekly list.

The quarterly quality control sample is to be analyzed as set out in Section 13(4).

Section 14 specifies the analytical requirements for quality control samples.

PETROLEUM REGULATION SECTION 15: TOXICITY TESTING

The "how to" protocols for toxicity testing set out in Section 5 of the general regulation also apply to this Section.

Section 15 of Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector requires dischargers to perform a Fish Toxicity Test and a *Daphnia magna* Acute Lethality Toxicity Test with process effluent and once-through cooling water.

For each process effluent sampling point, the tests are to be performed once in each calendar month on the same day as samples are collected for thrice weekly monitoring.

For once-through cooling water, the tests are to be performed once in each quarter on the same day as samples are collected for the monthly chemical monitoring of once-through cooling water.

Should three tests in a row, for process effluent, result in no more than 20% fish mortality, the frequency of fish toxicity testing can be reduced to once per quarter.

The frequency will revert back to monthly should mortality greater than 20% result in any of the once per quarter fish toxicity tests.

Daphnia magna testing remains at a monthly frequency throughout the 12 month monitoring period.

The Fish Toxicity Test (using rainbow trout) is described in the Ministry of the Environment document "Protocol to Determine the Acute Lethality of Liquid Effluents to Fish" (2).

The Daphnia magna Acute Lethality Toxicity Test is described in the Ministry of the Environment document "Daphnia magna Acute Lethality Toxicity Test Protocol" (3).

PETROLEUM REGULATION SECTION 16: FLOW MEASUREMENT

The "how to" protocols for flow measurement set out in Section 6 of the general regulation also apply to this section.

Section 16 of Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector specifies that there must be continuous flow measurement at a point representative of the flow at a process effluent sampling point.

Provisions are made under Section 16(2) for estimating total daily flow in the event that flow measuring equipment has malfunctioned, given that "...all reasonable care has been taken to avoid and correct the malfunction...".

Flow may be estimated or measured at the time of discharge or sampling for once-through cooling water, stormwater, landfarm leachate, and emergency overflows.

PETROLEUM REGULATION SECTION 17: REPORTING AND RECORD-KEEPING

All information which is considered by the discharger to be confidential business information must be so identified on each page.

Each discharger must provide, to the Director, copies of the Initial Report as set out in Section 17(1) of Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector within 3 months and 7 days of the filing of the regulation. It is requested that four copies of the Initial Report, including attachments, be provided.

Analytical results, flow measurement data, and malfunction information are also to be reported as outlined in Sections 17(3), 17(4), and 17(15), respectively.

In the malfunction information section, it is especially important to indicate where the malfunctions caused non-compliance with the regulation, that is, failure to submit data. The information on causes of malfunctions and remedial measures taken will be considered by abatement and enforcement staff in responding to violations.

Additional reporting requirements specific to the Petroleum Refining Sector Regulation include:

- reporting in writing to the Regional Director any changes to the information in the Initial Report within 30 days of the end of the month during which any such changes occurred (Section 17(2));
- submission of a sampling schedule for monthly, quarterly and characterization sampling, 30 days prior to the sample collection (Section 17(8)). This will provide Ministry staff the option of collecting their own audit samples or inspecting the plant's sampling procedures;
- quarterly reporting, in writing, to the Regional Director, of the quantities of chemicals added to once-through cooling water. This is required because the dosages are usually intermittent, and consequently the sampling program alone may not provide sufficient information on loadings;
- no later than 9 months after the start of the collection of samples (12 months after the reporting section comes into force), a report detailing the variation in daily flow for each process effluent stream. This information is required in order to determine if flow-proportional sampling will be required under the limits regulation.

Section 17 also outlines record-keeping requirements, which cover the following items:

- sampling times and procedures;
- maintenance and calibration of sampling equipment;
- analytical methods used.

Although each direct discharger is not required to report the above-listed information, it must be maintained and available should the Ministry request such information.

PETROLEUM REGULATION SECTION 18: TIMING

Section 18(1) states that Section 17 (Reporting) of the regulation comes into force on the first day of September, 1988.

All other Sections come into force on the first day of December, 1988.

The additional time was requested by industry to provide sufficient time to acquire and install sampling and flow monitoring equipment, to negotiate contracts with private laboratories, and to train staff.

Section 18(3) states that Sections 7 to 12 and 15 under Ontario Regulation 359/88: Effluent Monitoring - Petroleum Refining Sector will cease to apply on the first day of December, 1989. Section 5 (Characterization) and Section 6 (Daily Sampling) along with Section 17 (Reporting) will continue to apply under the regulation after the first of December, 1989.

PART TWO: THE MISA APPROACH TO EFFLUENT MONITORING

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BACKGROUND

ENVIRONMENTAL CHALLENGE

Ontario, like many industrialized areas, is facing the challenge of dealing effectively with the discharge of toxic contaminants to its lakes, rivers, and streams.

High mercury levels in fish, dioxin in the Niagara River, the perchloroethylene spill in the St. Clair River -- all have focussed attention on toxic contaminants and the potential risks they pose to aquatic life, public health, and drinking water quality.

In the past pollution control measures have emphasized traditional pollutants such as biodegradable wastes, suspended solids, ammonia, phosphorus, oil and grease, and phenolics. They have seldom addressed the toxic contaminants presently of greater concern.

The dilution capacity of abundant water was too often viewed in the past as a resource to be exploited. Attempts to control pollution were hampered by the perception that man-made materials and the organic wastes created by growing populations could be flushed away.

We know now that dilution cannot be considered infinite. Certain compounds pose a risk to fish, plants, wildlife and human beings even at low concentrations. This risk is particularly significant for persistent toxic contaminants because they either never break down or do so very slowly. Some may accumulate in the environment and are passed up the food chain in increasing amounts, resulting in increases which may be orders of magnitude higher in large fish than the levels present in the ambient water.

To eliminate these problems, toxic contaminants must be prevented from entering Ontario's waterways. MISA -- Municipal/Industrial Strategy for Abatement -- is Ontario's new control program designed to systematically reduce the discharge of toxic contaminants.

THE MISA INITIATIVE

The MISA program was officially announced by the Ontario Ministry of the Environment in the White Paper of June 1986 (4). The goal of the program is to reduce all municipal and industrial waste loadings and to virtually eliminate the discharge of persistent toxic contaminants to Ontario's waterways.

In this context, the Ministry considers virtual elimination of a persistent toxic substance to be reduction to a level as close to zero as is possible to measure contaminants.

To achieve the goal of virtual elimination, the MISA program has introduced new concepts and regulatory powers for pollution control. Legislative authority is provided by Section 136 of the Environmental Protection Act (5). Under this authority, the Ministry will impose monitoring and effluent limits regulations on all dischargers in Ontario.

The monitoring regulations will require dischargers to monitor their point source discharges at regular intervals. This will provide comprehensive data on effluent quality, particularly for toxic contaminants. Such a data base must accurately reflect all discharger operating conditions. The monitoring regulations, therefore, require sampling at various frequencies over an entire year and specify standard procedures for sampling analysis, quality assurance and quality control (QA/QC).

Industry's self-monitoring under the regulations will be subjected to an independent audit program carried out by the Ministry of the Environment.

Information generated by monitoring will produce a data base on contaminants discharged across Ontario. This data will be evaluated and then applied to the development of effluent limits. The limits will be established, based on the best available pollution control technology which is economically achievable (BATEA). A more detailed discussion of BATEA can be found in the MISA White Paper.

Where there are receiving water quality problems attributable to a specific discharger, more stringent water quality-based effluent limits will be established.

Periodic review of effluent limits will be carried out. New and lower effluent limits will be imposed as improved treatment technologies are developed, or if adverse effects on receiving water quality (resulting from discharges) are detected.

Through this process of on-going evaluation and step-by-step reductions, MISA's ultimate goal to virtually eliminate the discharge of toxic contaminants will be achieved.

Such a goal fulfills Ontario's commitment to the protection and improvement of our natural water resources. This goal is also consistent with the provisions of the Canada-Ontario Agreement Respecting Great Lakes Water Quality (6) and the Canada-United States Great Lakes Water Quality Agreement (7).

The MISA monitoring and limits regulations will first apply, on a sector-by-sector basis, to nine industrial sectors and the municipal sector. The nine industrial sectors are:

- Petroleum Refining;
- Organic Chemical Manufacturing;
- Pulp and Paper;
- Metal Mining and Refining;
- Industrial Minerals;
- Iron and Steel;
- Electric Power Generation;
- Inorganic Chemical Manufacturing;
- Metal Casting.

This group accounts for approximately two-thirds of Ontario's direct industrial dischargers. The remaining dischargers will be covered as other sectors are brought under regulation.

The Municipal Sector will consist of all sewage treatment plants in the province.

Dischargers to the municipal sewerage system constitute the indirect discharger group. This group will be regulated under the MISA Sewer Use Control Program.

The regulations are being developed with dischargers and public participation. Consultation with industries and municipalities is maintained through Joint Technical Committees (JTC), made up of representatives from the Ministry, Environment Canada, and the affected dischargers. These technical committees, one per sector, oversee studies during the pre-regulation phase and provide the opportunity for the dischargers to have input to the regulation development process.

Public review of the regulation is initially provided by the MISA Advisory Committee (MAC). Independent technical and environmental experts sit on this committee. MAC provides the Minister of the Environment with advice and comments on regulations being developed and other MISA matters.

All regulations will appear in draft form providing a 60-day period for public review and comment.

APPROACH

INTRODUCTION

This section provides the background rationale for the MISA monitoring requirements and discusses the overall monitoring strategy.

FROM MONITORING TO ABATEMENT

Information gathered during monitoring will provide, for the first time, a data base on the toxic contaminants discharged to Ontario's waterways. In addition to fulfilling Ontario's commitment under Great Lakes Water Quality Agreements, information will be made available to the public on the extent of pollution discharged to Ontario's waterways.

Most importantly, monitoring will serve in the process of developing effluent limits on toxic contaminants. The data generated by monitoring will first indicate the concentrations and total loadings of contaminants discharged by each industry and municipal sewage treatment plant. From this data and other information on wastewater treatment plant operation, the Ministry will determine which dischargers have the most effective treatment processes. This will be determined on the basis of effluent quality, reflecting both the level of chemical contaminants and the toxicity.

Several "candidate" types of treatment technologies in each sector may greatly reduce contaminant levels in their effluent. The candidate technologies and the corresponding effluent quality will then be compared to technologies designated as "best available technology" for that sector and its corresponding effluent quality in other jurisdictions, especially the United States. It was noted in the White Paper that the United States Environmental Protection Agency has developed regulations under the Clean Water Act which define BATEA for most industrial sectors. BATEA is based not only on end-of-pipe treatment, but may also include a variety of other measures such as manufacturing process change, substitution of less toxic chemicals, in-plant treatment and recycling where appropriate.

Other information will also be used in the comparison. Under certain conditions, similar technologies produce different effluent qualities. Differences in raw materials, manufacturing processes, and operating conditions, including climate, can affect effluent quality.

Economic considerations are essential to the process of defining best available technology economically achievable (BATEA). Capital and operating costs of various levels of treatment and operations will be identified.

From these technical and economic comparisons, the Ministry will determine the best available technology economically achievable for each sector. Dischargers will have input to this process through participation on the joint technical committees (JTCs). The corresponding effluent limits will then be set. The objective of the limit setting regulation is to achieve control of all contaminants of concern, in line with the goals of the MISA program. In practice, the objective will be achieved by monitoring a selected list of contaminants and setting numerical limits based on these. Limits may also be derived from other jurisdictions. The Ministry can set limits on any contaminant. The monitoring strategy is geared to identifying contaminants in effluents and to monitoring these at high frequencies. The program has the flexibility to revise the frequency of sampling, as information becomes available during the regulation.

The information collected during the monitoring phase will give advance warning to the dischargers and the Ministry concerning dischargers which would be out of compliance with future limits. When the limits regulations are in force, industries and municipalities which are out of compliance will have to undertake abatement action.

In addition to the BATEA limits set on discharges, the Ministry will require the use of "best management practices" (BMPs) to control releases of toxic pollutants from plant runoff, spillage and leaks, waste disposal sites, and drainage from raw materials. Monitoring data will be used to determine the need for control and point to specific practices for consideration as BMPs. The Ministry will work with industry to develop "best management practices" that will more effectively detect and control leaks and spills. Continuous on-line monitors are currently used in some industries for detecting spills.

The Ministry wishes to proceed to the abatement stage of MISA as rapidly as possible. However, a minimum of twelve months of treatment operating data are needed to define the performance of the existing technologies allowing for different industrial manufacturing process conditions and seasonal climatic effects.

THE MISA MONITORING STRATEGY

A large number of chemicals are manufactured and used in today's industrial society. It is impractical to monitor for all chemicals used and released to the natural environment. A system must, therefore, be in place to evaluate chemicals to be monitored by specific sectors. In addition, the range of allowable monitoring techniques must be limited to provide a common scientific basis for comparison of data from sector-to-sector and from site-to-site.

An overall monitoring approach is being followed which is briefly described below:

- development of the Effluent Monitoring Priority Pollutants List (EMPPL), in order to identify the toxic contaminants of concern;
- pre-regulation consultation and monitoring, which will facilitate identification of specific chemicals to be monitored at different frequencies and appropriate techniques for chemical and toxicity measurements;
- definition of regulation monitoring requirements based upon input from the two above-noted steps.

The requirements for compliance monitoring under the limits regulations will be tailored to the specific contaminants of concern for each sector. A regulatory mechanism to add or delete chemicals for monitoring, or to modify monitoring frequencies, will be applied.

Each of the above steps is described in more detail in the following subsections and presented schematically in Figure 1.

EFFLUENT MONITORING PRIORITY POLLUTANT LIST

There are some 30,000 chemicals produced or used in Ontario. As noted earlier, the Ministry developed a screening process to identify a list of contaminants of greatest concern for Ontario. This list, the Effluent Monitoring Priority Pollutants List (EMPPL), is supported by a published document (8).

The Ministry's screening process consisted of a chemical identification stage and a preliminary hazard assessment stage.

During the identification and assessment stages, a number of factors were considered about each chemical, including the chemical's:

- potential presence in effluents discharged to Ontario's waterways;
- environmental persistence;

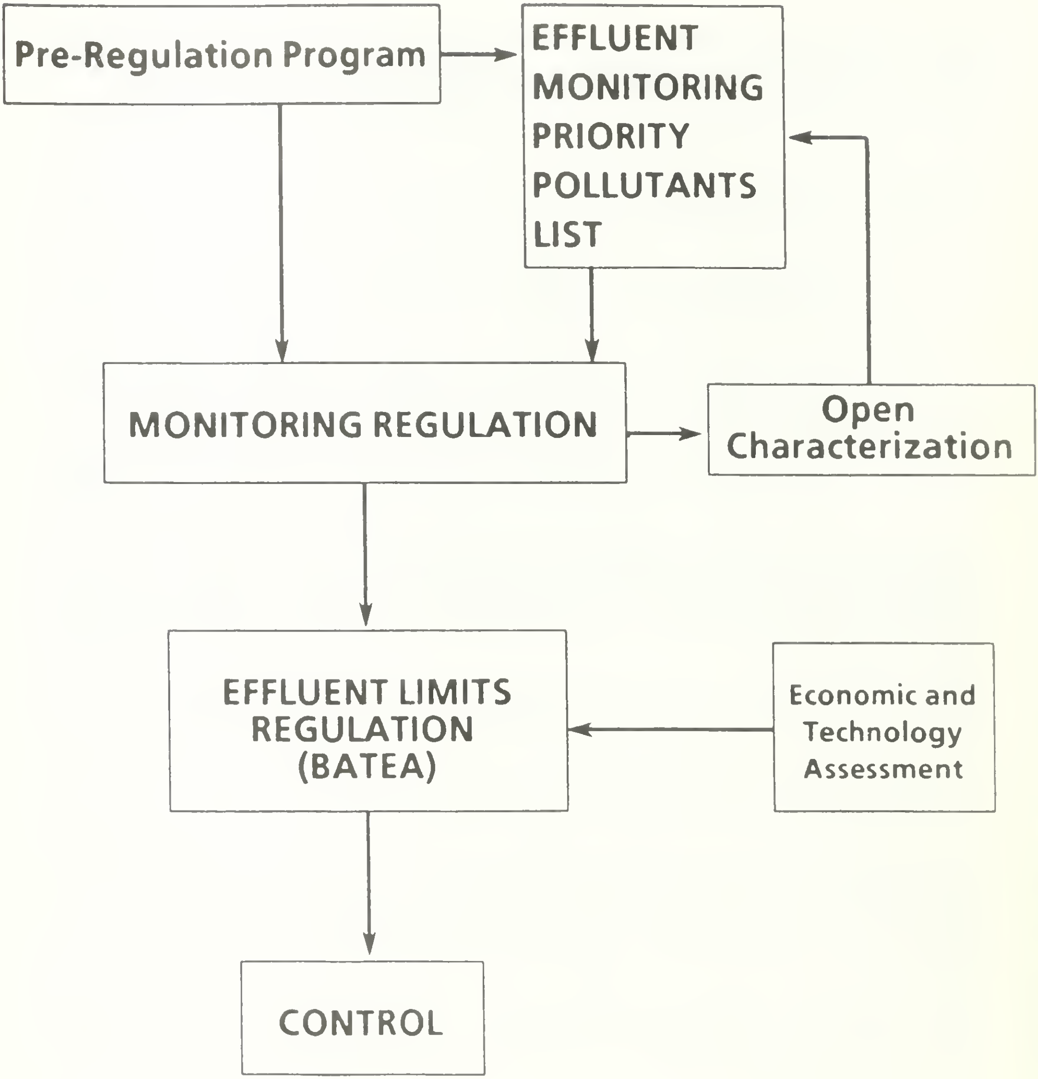
Pre-Regulation Program
EFFLUENT MONITORING PRIORITY POLLUTANTS LIST
MONITORING REGULATION
Open Characterization
EFFLUENT LIMITS REGULATION (BATEA)
Economic and Technology Assessment
CONTROL

Figure 1
MISA REGULATORY APPROACH

- potential to bioaccumulate;
- acute and sub-lethal toxicity to biological organisms, including humans, as measured by specific indicators of toxicity such as the ability to induce tumours and affect successive generations.

The current EMPPL (1987) includes 179 chemicals or chemical groups derived from an assessment which considered 1500 chemicals.

A subset of EMPPL was used in developing sector characterization lists for each sector. Only 133 of the 179 chemicals currently have proven and accepted analytical procedures. The Ministry Laboratory Services Branch is responsible for developing methods for the remaining contaminants. When such standard techniques are available for the remaining contaminants, the characterization lists for each sector will be updated.

The hazard assessment process is ongoing. Chemicals not on the current EMPPL but identified through open scan characterization will be candidates for screening and subsequent inclusion on EMPPL. Chemicals may also be added to reflect new environmental fate or toxicity information. EMPPL will continue to serve as the basis for developing regulations.

THE PRE-REGULATION PROGRAM

Pre-regulation programs are being undertaken voluntarily by plants in each sector to provide an initial data base on which to build the sector specific requirements for the monitoring regulations. These programs include:

- collection of information covering several areas of plant operations from process descriptions, raw material use, to sewer diagrams and effluent treatment information;
- site visits by multi-disciplinary teams to inspect on-site operations and general environmental control practices, sampling, and flow monitoring locations; in some cases engineering consultants have been hired to assist in this task;
- pre-regulation monitoring programs following sampling and analytical protocols provided by the Ministry;

- review of other data bases such as:
    - i) MOE open characterizations
    - ii) historical MOE and Environment Canada monitoring data
    - iii) MISA Pilot Site Program studies
    - iv) Environment Canada studies such as the Upper Great Lakes Connecting Channel Studies (UGLCCs) (9,10,11) and The Niagara River Toxics Study (12)
    - v) company supplied monitoring and chemical use data
    - vii) the published literature on process effluent contaminants from similar sources
- development of sector-specific monitoring lists. The sector lists are subsets of EMPPL: compounds on EMPPL but not found on the sector list were excluded because these contaminants would not be present in effluents of that sector, or there are no standard analytical methods for some compounds.

PRINCIPLES OF THE MONITORING REGULATION

Under the MISA program, limits will be based upon both loadings and the concentrations of contaminants present in effluents. These will be derived from long term performance of treatment processes, as given in annual and monthly averages, and will specify a daily maximum limit to control variations in performance caused by day to day operational conditions and normal manufacturing process cycles.

It is important that the information gathered during monitoring presents a representative measure of effluent quality. Inaccurate, unreliable data could lead to incorrect conclusions and inappropriate actions.

The monitoring program, therefore, has been designed to ensure the following conditions are met:

Firstly, all monitoring data must be of known and acceptable quality. The QA/QC requirements specified in the MISA regulations are designed to ensure acceptable data quality. A system of procedures and documentation is prescribed for all monitoring activities including sampling techniques, sample preservation, analytical procedures, and data reporting. The regulation prescribes the minimum QA/QC data that is to be generated and requires that all such data be reported to the Ministry.

Secondly, to ensure that the data reflects the variability of the effluents, dischargers are required to monitor during all operating conditions, including normal and upset, in all seasons of the year.

Finally, a sufficient volume of data must be generated to provide a statistically valid data base for the development of limits. The Ministry is examining approaches for addressing the statistical analysis and reporting of data at or below method detection limits (MDLs).

Types of Effluent Streams

The MISA monitoring program is directed at all potential point sources of pollution entering surface watercourses, including treated or untreated process effluents, cooling water, stormwater runoff, emergency overflows, waste disposal site drainage, and combinations of the above. These types of effluent streams are shown on Figure 2 and described below:

1. **Process Effluents**, with or without treatment, are the primary concern of the MISA program since they contain the highest concentrations and loadings of contaminants. The monitoring strategies are most comprehensive and rigorous for these waste streams.

2. **Cooling water** is used to cool industrial process units and can be contaminated by leaks. In addition, chemicals are added to control slime growths and prevent corrosion.

3. **Stormwater runoff** following rainfall or snowmelt events can carry contaminants from processing or storage areas. Storm drainage channels are often the route for leaks and spills to gain access to surface waters.

4. **Waste Disposal Site** drainage exists on-site in some industries that treat or dispose of solid waste on their own property.

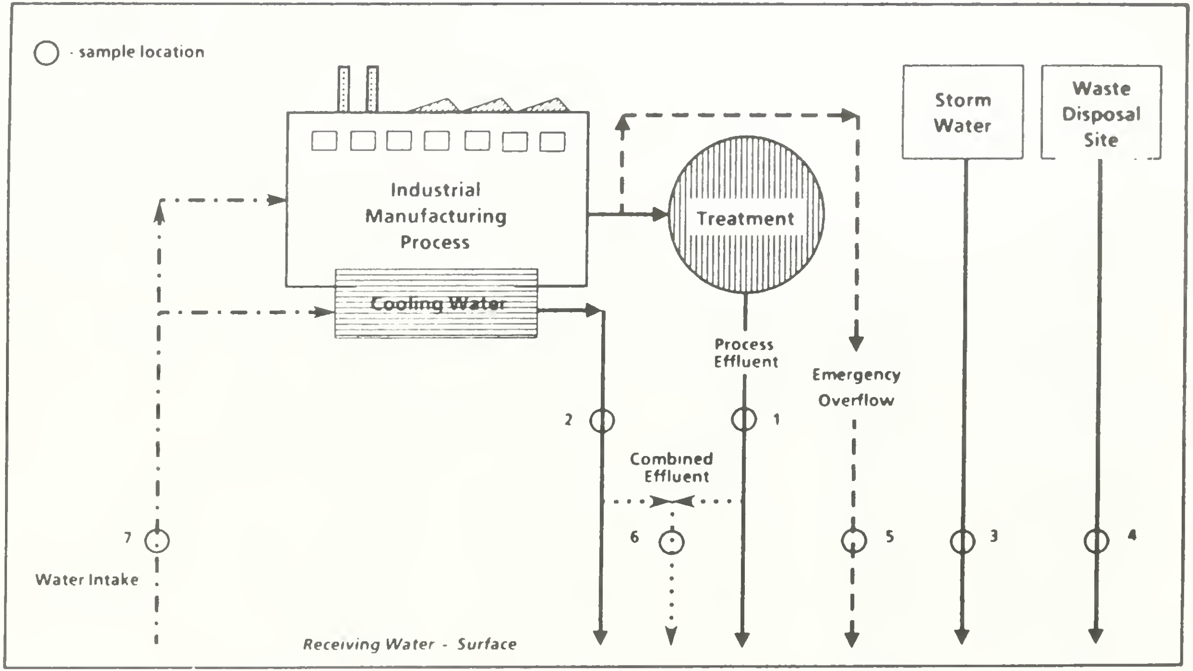

Figure 2 - Typical Industrial Plant Site Monitoring Locations

5. **Emergency Overflow** routes often exist for untreated or partially treated wastewater. These are used only when treatment processes or equipment breaks down.

6. **Combined effluent**, for the purposes of these regulations, consists of process effluent mixed with cooling water and possibly other wastewaters.

7. **Intake Water** locations are not required to be sampled in the MISA program; however, any plant may submit data from these locations. Intake water can be contaminated as a result of polluted sediments from historical releases, upstream contamination, and recirculation of discharges from the plant site.

MONITORING FREQUENCIES

The Ministry's approach to monitoring reflects both the need for a comprehensive data base, and the limitations posed by practical considerations including cost.

Frequent monitoring (eg. daily, three times weekly, weekly) by dischargers will be required for a short list of parameters.

Less frequent monitoring (eg. monthly, quarterly, annually) by dischargers will be required for a long list (eg. the sector characterization list) of parameters in order to identify contaminants of concern.

These parameters will be considered as one source of information in developing control limits.

The regulation specifies monitoring frequencies for each type of effluent stream and lists the contaminants which must be monitored at the frequency specified.

Daily Monitoring For Process and Combined Effluents

Daily monitoring applies mainly to process and combined effluent streams. Monitoring at this frequency is required for a short list of parameters which serve as indicators of treatment performance.

Specifically, the information from daily monitoring will be used to:

- provide a record of parameter variability including manufacturing process load variations, treatment plant upsets, and spills;

- provide accurate daily maximum and monthly average loadings and concentrations;
- aid in determining if a plant is operating efficiently and consistently in relation to potential BATEA limits.

On-line continuous monitoring of some key parameters may be an alternative to daily monitoring. Although requirements in the regulations call for only mean, maximum, and minimum values to be reported, the data retained at the plant site could provide an uninterrupted record of the plant's performance.

Parameters are chosen for daily monitoring if they fall into one or more of the following categories:

- always present in measurable quantities;
- currently monitored at this frequency to meet previous guidelines, regulations, or site specific control documents such as Control Orders or Certificates of Approval;
- needed for daily operational control of the treatment plant, to assure the Ministry that the likelihood of release of contaminants of concern is reduced.

Three Times Weekly Monitoring For Process and Combined Effluents

Thrice weekly monitoring will be used to generate a statistically supportable data base on a list of contaminants longer than but including the daily monitoring list. Where the variability of effluent quality is unknown, this frequency is estimated to be the minimum necessary to calculate representative monthly average loadings and concentrations with acceptable confidence limits.

In addition, since monitoring is undertaken almost every second day, the data can be used to assess whether the parameters being monitored are suitable as indicators of treatment performance.

Specifically, this data will be used to:

- calculate monthly loadings and concentrations;
- provide a record of parameter variability including manufacturing process load variations, treatment plant upsets, and spills;
- establish a basis of comparison for parameters monitored at other frequencies;
- aid in identifying parameters that require control and point to appropriate treatment technology;

- provide a basis for comparison of plants within the sector;
- establish a basis for inter-sector comparisons of loadings for these parameters;
- aid in identifying well operated plants which consistently control toxic contaminants and which could be considered as benchmarks for designation of BATEA technologies;
- establish the performance of plants in comparison to BATEA designated plants and to EPA reference limits;
- establish the suitability of controlling these parameters;
- be used as a basis for altering the monitoring frequencies;
- relate dischargers to actual or potential water quality impacts.

The parameters chosen for this frequency of monitoring meet one or more of the conditions listed below; the parameters are:

- frequently present in effluent, based on site monitoring or literature reviews of similar plants or sectors;
- potentially present in effluent based on their presence in raw or partially treated wastewater, or common use at the site;
- deleterious in the aquatic environment, and have had detrimental impacts at that site in the past;
- currently monitored at this frequency because of an existing guideline, regulation, or control document;
- representative of other toxic contaminants and groups monitored less frequently.

Weekly Monitoring Frequency For Process and Combined Effluents

Weekly monitoring will provide an estimate of contaminant variability over the long term. It will also be used by the Ministry to evaluate the need for control of traditional contaminants, such as oil and grease. In the absence of knowledge of the variability of effluents, this frequency of monitoring may be inadequate for the derivation of BATEA limits. It may be used, however, for discharge parameters, which are relatively invariant in effluents, or for which the Ministry already has sufficient data to estimate variability.

Contaminants selected for weekly monitoring meet one or more of the following conditions; the parameters are:

- traditional parameters which are already monitored at this frequency;
- those for which the Ministry requires only estimates of annual or monthly loadings; for example the reporting of phosphorus discharges for the purposes of compliance with agreements with other jurisdictions.

Monthly Monitoring Frequency For Process and Combined Effluents

Monitoring for a longer list of chemicals is required on a monthly basis. The Ministry will use data from this level of monitoring to establish the presence or absence of contaminants of concern.

The data from this monitoring will be used to:

- estimate annual loadings for those contaminants routinely present;
- show whether particular toxic contaminants monitored more frequently are representative of corresponding groups of toxic contaminants; if the relationship is confirmed, the Ministry may be able to demonstrate that the control of the representative toxic contaminant will provide control of the whole group;
- identify contaminants of concern which may require more frequent monitoring;
- provide information on the presence of toxic contaminants to be considered with the monthly toxicity testing results;
- relate receiving water, biota, and sediment contamination to sources.

Contaminants are included in monthly monitoring for the following reasons; the contaminants are:

- detected infrequently in effluents;
- potentially present in effluents by virtue of their use on site;

- members of a group of contaminants in which at least one other member meets the above criteria;
- members of a group of contaminants in which at least one other member is monitored more frequently (weekly, thrice-weekly, daily).

Characterization and Open Characterization

Characterization is carried out in order to determine the presence or absence of contaminants of concern. Frequent detection of contaminants of concern through characterization may result in a requirement for increasing monitoring frequency.

The purpose of open characterization is to identify the presence of any contaminant not currently on EMPPL, but which may potentially be a contaminant of concern. Contaminants frequently detected as a result of open characterizations may lead to assessment of these contaminants for inclusion on EMPPL.

The characterization of effluents describes their chemical composition by applying analytical techniques to the identification of organic and inorganic chemicals. The analytical technique specified in the regulations for the identification of most organic compounds is Gas Chromatography-Mass Spectrometry (GC/MS). Various analytical techniques including Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Emission Spectroscopy (ICPES) are applied to the identification and quantification of inorganic chemicals.

The MISA Effluent Monitoring program uses three approaches to characterization:

- characterization for a list specific to each sector ('closed' characterization for a sector specific list);
- characterization for the Ontario Effluent Monitoring Priority Pollutant List (full characterization for the entire EMPPL);
- open characterization which includes full characterization for the entire EMPPL and a full scan identification of organic compounds and inorganic chemicals.

Note: The General Regulation defines "characterization" to be analysis for all substances identified in Schedule 1, which includes the entire EMPPL, for which analytical techniques currently exist, and traditional pollutants.

Characterization and full characterization of an effluent consists of the determination of presence or absence for each pollutant on either the sector list or the full EMPPL and provides measurements for each pollutant to the method detection limits specified. The frequency of characterization or full characterization may vary from monthly to annually, based on the prior availability of data for each sector or plant. In addition, characterization would be required after major process changes or the introduction of new raw materials or products. Plants which routinely alter their production cycles may be required to characterize their effluents at greater frequency.

The information from characterization and full characterization can be used to determine the frequency of occurrence of known contaminants of concern (EMPPL). The concentrations at which these are detected and the frequency of their occurrence may trigger more intensive monitoring.

The Ministry accepts that low frequencies of characterization will provide meaningful data only in the long term. Higher frequencies, for example, monthly analyses providing 12 results per year would assure the probability of detection of a contaminant at least once at greater than 99% when the likelihood of presence above the method detection limit is at least 50%. At a lower likelihood of presence, for example, 10%, the corresponding probabilities of detecting a contaminant at least once are reduced to approximately 70%.

The Ministry suggests that six (6) characterizations be the frequency for a reasonable probability of detection at least once, for contaminants frequently present, that is present 50% of the time or greater. This provides a probability of 98% that the contaminant will be detected at least once. For contaminants infrequently present, that is 10% of the time, six characterizations will have approximately a 50% probability of detection.

Open characterizations will be performed to identify contaminants which may be present in the effluents which are not included on EMPPL. In open characterizations, gas chromatography/mass spectrometry is used to identify the organic chemicals and ICPES is used to identify the inorganic chemicals. Both procedures provide measurements of concentration.

Organic chemicals will be identified with the aid of a computerized library search of mass spectra listings (e.g. National Bureau of Standards Library). The requirements for positive identification are prescribed, and include defined criteria which sample and library spectra must meet, before the compound is considered identified. The spectroscopist initiates a search using a computer program which matches the sample spectrum with the spectra in the electronic library. The match is rated according to a scoring system in which 1000 points constitutes a perfect fit for each of a number of criteria. A positive identification requires comparison with the spectrum of a reference standard and a match of at least 800 points in 1000 for each of the specified criteria. In some cases, a value of 700 may be permitted. Further interpretation depends on the experience of the spectroscopist and the history of the sample.

Unknown peaks may also be identified by interpretation by experienced spectroscopists from first principles, that is knowledge of chemical structures and their corresponding mass spectra. This results in the provisional identification of the compound or identifies the group of chemicals to which the compound belongs. However, positive identification of the unknown compound still requires comparison with a reference standard in accordance with the above criteria.

The Ministry will conduct open characterizations (including the full EMPPL) at least once each year as part of its audit program.

Dischargers would be required to conduct more open characterizations either where the effluents are known to contain large numbers of chemicals, not on EMPPL, or where the nature of the effluents is largely unknown.

The total number of characterizations and open characterizations which may be required under the monitoring regulations will vary from sector to sector. The requirements will be based on the number of each type of analysis performed during pre-regulation monitoring, and the availability and quality of historical data.

The Ministry will ensure that a minimum of six characterizations are available prior to the development of the effluent limits regulation for each discharger. At least two of these will be required to be carried out by the discharger in the monitoring regulation for each sector. The other four may consist of pre-regulatory characterizations provided by the Industry, and the ministry audit sampling program during the regulation.

The requirement could be increased for plants that frequently change their manufacturing materials or processes and may have effluents with greater variability.

Cooling Waters

Once-through cooling water is not intended to come into contact with process streams. Contaminants may be present in once-through cooling water as a result of:

- contamination of the intake waters;

- leaks from process in the heat exchanger;
- spills into open channels;
- the addition of chemicals used as slimicides, algicides, or anti-corrosives;
- direct discharge of contaminated streams such as boiler water blowdown.

A monthly monitoring frequency is appropriate for cooling waters to aid in detecting long term leaks and those spills or discharges which occur frequently and have a continuous impact.

The regulation also requires that dischargers report periodically on the chemicals and their amounts added to the cooling water streams.

The monitoring list for cooling waters will include any parameters from the sector specific list that are:

- used as raw materials, process or product chemicals or indicators of these;
- directly added to cooling water.

Event Sampling for Emergency Overflows, Stormwater Runoff and Waste Disposal Site Effluents

The purpose of monitoring these sources is to identify the frequency and magnitude of these events and where possible to obtain an estimate of loadings. The Ministry will use this information to determine whether more intensive monitoring or corrective action is required.

A. Retention ponds which retain a storm water runoff for subsequent controlled release must be monitored each time there is a discharge from the pond to the environment. A sample must be taken and the flow estimated to determine loadings.

Dischargers without retention ponds will be required to take a sample during one runoff event each month when there is a rainfall event which exceeds 5 mm and to estimate the flow at the time of sampling. In some cases, sampling of runoff resulting from snowmelt may also be required in order to establish the magnitude of this source. The data will not be sufficiently comprehensive to determine loadings but will be used to aid in problem assessments.

B. Retention ponds which are not controlled, and discharge in each storm event are to be treated as storm sewers.

The regulation requires that waste disposal site effluents (including landfarms in the petroleum refining sector) be monitored during each discharge.

The regulations require dischargers to monitor emergency overflows during each overflow event.

The information generated from event monitoring will be used to:

- compare industrial stormwater contamination levels. The Ministry will establish background levels of contamination anticipated in any runoff by examining historical levels of contaminants observed in urban stormwater runoff in Ontario; significantly higher levels in industrial runoff may trigger remedial action including implementation of best management practices;
- estimate loadings when total flow information is available, otherwise only an instantaneous loading rate can be calculated;
- relate concentrations or loadings to rainfall events;
- identify the frequency and magnitude of waste disposal effluent discharges and emergency overflows;
- assess the need for specific "best management practices" or other remedial actions.

The contaminants included on an event monitoring list will include those parameters which:

- are used on site as raw materials or in process operations;
- serve as indicators of these chemicals;
- have been detected in waste disposal site sludges.

SAMPLING REQUIREMENTS

To ensure that data of proven quality are obtained from the samples collected during monitoring, sample collection and preservation must be rigorously controlled.

Sample Collection

The sampling of process effluents prior to dilution is to be preferred. When this is impractical, combined effluents will be sampled, recognizing that the presence of contaminants may be masked through dilution or interaction with the contaminants from other streams.

For process and combined effluents, samples are to be collected at points where the effluent has not been diluted by cooling water or other less concentrated streams to a degree that would cause significant masking of the contaminants and result in levels below method detection limits.

Samples from these streams must be representative of the effluent over time. Therefore, the regulation stipulates that automatic flow-proportional or equal time/equal volume composite samples be taken. Flow proportioned samples are preferable, and are required for process effluents when flow is variable. Variable flow is defined in the general regulation.

Sampling locations should be placed where thorough mixing in the cross-section takes place. The sampling locations will be identified by the Ministry of the Environment through site visits and in consultation with plant staff. The criteria for selection of the sampling locations include:

- effluent homogeneity;
- stream velocity;
- accessibility;
- practicability.

The intake tubing for automatic samplers should face into the stream at approximately two-thirds the depth of the effluent discharge channel, with intake velocity of approximately 1 metre per second to give representative samples especially where suspended solids and associated contaminants may affect results.

For other effluent streams, such as once-through cooling water, stormwater runoff, waste disposal site effluent, landfarm leachate, and emergency overflows, grab samples may be taken.

Sample Preservation

Sample preservation protocols have been specified for all parameters that are susceptible to degradation through chemical, biological or physical interactions. These protocols range from the addition of a chemical preservative (i.e., acids, bases, inorganic or organic chemicals) to simple refrigeration and storage criteria.

These protocols are drawn from techniques recommended by agencies including the Ministry, Environment Canada, U S

Environmental Protection Agency and the American Public Health Association as suitable to preserve sample and analyte integrity.

FLOW MEASUREMENT

In order to assess the full environmental impact of an effluent, it is necessary to determine the total amount of contaminants, or loadings, discharged to the receiving water. Therefore, under MISA, monitoring data must provide information on both the concentration of contaminants and the flowrate of effluent streams. Concentrations are determined by sampling and analysis of the effluent. Loadings are calculated by multiplying the concentrations by flowrate.

For process and combined effluents, the regulation specifies that flow measurements must be taken continuously and accurately. This reflects the Ministry's expectation that the highest concentrations and loadings of parameters to be monitored are found in these streams.

For emergency overflows, stormwater runoff, and cooling water streams, flow measurement can be estimated at the time of sampling. If a stormwater retention pond is used, the volume of discharge may be estimated by the change in the volume of the pond contents after release.

To ensure that these readings are precise and representative, the regulation specifies the frequency and defines the acceptable limits of accuracy for flow measurement on each type of stream.

Flow measuring systems in most instances consist of a primary measuring device, which establishes the relationship between flowrate and a measured variable, and a secondary measuring device, which converts the measured variable to a flowrate in volumetric units.

Primary measuring devices which have documented accuracies of plus or minus 5 per cent of reading over a range of 20 to 100 percent of full-scale flowrate will be deemed to perform to that accuracy if installed according to recommendations and guidelines contained in the development or standard documents for the device. These devices are suited for the measurement of process effluent flowrates and have been accepted world wide by various standards organizations such as British Standards (B.S.), International Standards Organization (ISO), American Society for Testing and Materials (ASTM), and the National Bureau of Standards (NBS).

Secondary measuring devices are the instrument systems that acquire measured variables from the primary measuring devices by various sensing techniques and convert these variables into flow rate information in volumetric units. Recent published surveys have shown that virtually all secondary measuring devices are capable of accuracies of plus or minus 2 percent of full-scale or better.

The combined accuracy of the primary and secondary measuring device for flow at process outfall, calculated as worst case accuracy, is plus or minus 7 percent of actual flowrate at 100 percent of full-scale and plus or minus 15 percent of actual flowrate at 20 percent of full-scale. Continuous operation of a flow measurement system below 20 percent of full-scale is only permitted if it can be demonstrated that flow measurements are accurate to plus or minus 15 percent of actual flowrate.

The accuracy of flowrate measurements for cooling water and storm water outfalls has been set at plus or minus 20 percent of actual rate. In many cases methods and devices with much better accuracy can easily be implemented, or may already exist, especially on cooling water lines.

ANALYTICAL REQUIREMENTS

Analytical principles are provided for the analysis of all samples. Adherence to these principles will ensure that the data generated by analysis are reliable, are of consistent quality and are sufficiently compatible to be integrated into a valid and meaningful data base.

To develop the analytical protocols, staff from the Ministry and Environment Canada reviewed both the literature and current internal methods, and consulted with technical staff from government, industry, and the public.

The resulting protocols in the regulation are sufficiently prescriptive to ensure consistent results but, at the same time, are flexible enough so that different laboratories can apply them to different situations. This flexibility will also allow for the analyst's discretion and for the incorporation of new technology within the confines of internationally accepted and recognized principles.

The principles apply to both the preparation of samples and to the analytical procedures. Good laboratory procedures will effectively reduce interferences which would distort sample analytical results.

The principles of instrumental measurement allow laboratories to follow methodologies used by the Ministry, Environment Canada or the US EPA. Other methodologies can also be used as long as the appropriate principles are maintained.

Under the monitoring regulations, laboratories will be required to provide the analytical method detection limit for each parameter before samples are analyzed. The procedures for determining method detection limits are provided in a Ministry publication titled "Estimation of Analytical Method Detection Limits (MDL)"(1).

The analytical method detection limits (MDLs) for analytical test groups 16-20 which appear in the General Regulation are interim values only. Compound specific MDLs will be determined for the Volatiles and Extractables, Base Neutral and Acid (Phenolics) using Ministry and industry generated data through the procedure outlined in the Ontario Ministry of the Environment publication entitled "Estimation of Analytical Method Detection Limits (MDL)" (1). These MDLs will replace the interim values, listed in Schedule 3 part b, within 5 months of the date of promulgation of the Petroleum Regulation (that is, one month before the monitoring under the regulation takes effect). The compound specific MDLs will be as close to 1 ppb as possible, but will reflect the analytical variability associated with each parameter.

TOXICITY TESTING

Toxicity testing is used to assess the potential impact of complex effluents on the aquatic environment. In acute lethality toxicity testing, aquatic organisms are introduced to several dilutions of effluent starting with undiluted effluent. A survival rate of 50% or more among the test population, exposed to undiluted effluent over the test period, designates the effluent -- by convention -- as non-lethal. Non-lethal effluents are considered less likely to produce adverse impacts in the environment after dilution. Effluents designated lethal by these tests are considered more likely to have measurable environmental impacts.

The results of toxicity testing will be used to:

- establish a data base on the actual numerical median lethal concentrations (LC_{50}) of each effluent discharge with a view to limit setting based on the rainbow trout test;
- assess the potential impact of complex, whole effluents on the environment;

- provide interpretation, where possible, about chemical analytical results on samples taken at the same time;
- assess the capability of treatment to detoxify lethal waste streams;
- provide base-line operational data for the evaluation of benefits derived from the later implementation of treatment.

Because the tests are performed under standardized laboratory conditions rather than in the receiving environment, the results are not influenced by site specific environmental variables. The results can therefore be compared from site to site.

Two toxicity tests will be required under the monitoring regulations for each sector.

Rainbow Trout Acute Lethality Testing

The Rainbow Trout Test is the standard lethality test in Ontario. Several industrial dischargers in Ontario have been given effluent limits based on this test under control documents in Ontario legislation. An effluent is considered acutely lethal if 50% or more of the rainbow trout die when kept in undiluted effluent over 96 hours.

The rainbow trout has been traditionally used in Canada for aquatic toxicity work because it is readily available from local hatcheries, it can be easily maintained under laboratory conditions, and it is a sensitive, important fish species representative of cold water environments.

Trout are comparatively large aquatic organisms, and may not be killed by trace levels of priority pollutants over the test period. Survival may be due to detoxification by the test fish themselves or to loss of toxic potency prior to lethal impact on the fish due to the large volume of the fish compared to its surface area. The bio-accumulative potential of effluent components is not measured or predicted. The large size of rainbow trout at maturity does not allow for the use of this single species in life cycle testing.

Daphnia magna Acute Lethality Test

The Ministry is implementing a MISA Advisory Committee recommendation, supported by other technical reviewers and by the global literature, to require the performance of a 48 hour Daphnia magna acute lethality test in addition to the standard fish test.

The _Daphnia_ organisms (small water fleas) are often more sensitive than rainbow trout. Their smaller size makes them more suitable to the testing of low level toxic organic compounds, because, for example, their higher surface to volume ratio allows for more rapid equilibration to the test solutions.

Daphnia testing is inexpensive, fast, and simple, and requires less effluent volume, laboratory space, and equipment. _Daphnia_ testing is well established internationally.

Daphnia testing, because of the smaller test volumes required, may facilitate development of continuous flow testing methods of effluents, another MISA Advisory Committee recommendation which is consistent with Ministry planning. _Daphnia_ testing will not, however, be used initially for establishing whole effluent toxicity limits at the end of the pipe. The Ministry is not considering the application of whole effluent, end-of-pipe limits based on _Daphnia_ testing at this time.

The data may be useful in evaluating the impact of the discharge of persistent toxic contaminants on receiving waters and could be compared to the data base on rainbow trout.

REPORTING

The monitoring regulations require dischargers to collect information on their operations, and monitoring data from their effluents, and to provide this information to the Ministry. The reporting section of the regulation specifies report type, content, timing and format.

Each discharger must provide an initial report to document the steps the discharger will take to comply with the regulation and provide background information on the plant processes and operation. The report will subsequently aid the Ministry in the interpretation of monitoring results when effluent limits are developed.

Dischargers will also be required to provide on-going reports of the monitoring data including chemical analyses, flow ,and the results of toxicity testing. The reporting period is specified with more time allowed for the submission of data from complex analytical tests.

Both electronic and hard copy (paper) versions of the data will be required. The electronic copy is required to facilitate rapid and accurate transfer of data into Ministry computerized data bases. The hard copy, including the signed submission form, constitutes the data in legal terms.

Dischargers may also, if they wish, report intake concentrations and flow. The collection and analysis of this information must comply with the analytical, sampling, and quality control procedures specified in the regulation for process and combined effluents. The Ministry is prepared to consider net loadings based on a set of criteria, which are to be developed, and on a case-specific basis only.

The Ministry District Office receiving the submissions will check the information for completeness before accepting it. Errors or omissions will be followed up with the discharger and provisions made to resubmit the data. Monitoring information collected under the regulation will be available to the public. Confidential information will be retained in secure files subject to conditions of the Freedom of Information and Protection of Individual Privacy Act.

MINISTRY AUDIT

The purpose of the audit program for the regulatory phase of MISA is to verify that the self-monitoring data generated by dischargers is representative of the chemical loadings to the environment. As well, the audit program will test the reliability of the self-monitoring approach to produce data that are acceptable for abatement and enforcement actions.

The Ministry will carry out periodic inspections of sampling and flow measurement equipment and technique. In addition, the Ministry will, at unscheduled times, sample and analyze effluents for:

- parameters included on the characterization lists;
- any other organic compounds which can be identified through gas chromatography/mass spectrometry;
- and elements identifiable through an elemental scan.

ENFORCEMENT

Failure to comply with the regulation is a violation of the Environmental Protection Act and is considered an offence. Violations could be detected either by on-site inspections as part of the audit program, or as a result of the failure to provide the information required by the reporting section. Violations could lead to prosecution.

GENERAL AND SPECIFIC REGULATIONS

Under MISA, the monitoring requirements for any sector are expressed in two regulations. The first is a generic regulation which expresses the technical and scientific principles of monitoring applicable to all dischargers. The second regulation applies to a given sector and states specifically how those monitoring principles must be applied.

The regulatory monitoring requirements for any sector will be expressed in two complementary regulations: a general monitoring regulation and a monitoring regulation specific to each sector.

The general regulation provides the background implementation principles for monitoring which are common to all sectors. These include sampling and analytical requirements, procedures for toxicity testing, flow measurement requirements, and reporting procedures.

The Ministry stated these common requirements in a separate regulation as a convenient method of identifying those principles of science which are less likely to require extensive discussion during joint industry-government negotiations. With these principles clearly delineated, all sector negotiations can build from a common foundation and focus on sector-specific issues.

Whereas the general regulation provides the background principles, the sector-specific regulation states the actual parameters for monitoring and the monitoring frequencies for each sector. Parameters and frequencies are provided for each type of monitoring required including characterization, routine chemical monitoring, toxicity testing, and flow measurement. Regulatory requirements for reporting are also stated.

THE PETROLEUM REFINING SECTOR

THE PETROLEUM REFINING SECTOR

The petroleum refining sector is relatively homogeneous. The operation of refineries, including process descriptions and products, is well documented and understood. Although refinery processing primarily rearranges the structure of hydrocarbon molecules, it does not generally involve the addition of other substances (such as chlorine) to feedstocks to create entirely dissimilar derivatives. It is therefore logical to assume that studies carried out at selected refineries may be applicable to other similar operations, within limits.

The Ministry recognizes the substantial accomplishments of the Ontario petroleum refining industry in pollution control. Secondary (biological) treatment, dissolved air flotation and oily water separation have been installed at all Ontario petroleum refineries, bringing the refineries to, or very close to, BATEA as defined for this sector by the Environmental Protection Agency in the United States (US EPA). These facts, along with the availability of the data described in Section IV, were primary considerations in the Ministry's decision to formulate regulations for the petroleum refining sector first and to use those regulations as a framework for the other sectors.

THE PETROLEUM REFINING SECTOR IN ONTARIO

Description

The petroleum refining sector in Ontario consists of seven plants, six of which are conventional petroleum refineries with total annual sales of 24 billion litres, and one which is a petroleum-based producer of primary petrochemicals with a capacity of 1.3 billion kilograms.

The refineries' principal feed stock is crude oil from Western Canada. Crude oil is a mixture of thousands of different compounds and varies significantly in composition and physical properties, depending upon its source. There are two principal types of crude oil, natural (as found in underground formations) and synthetic (as produced by extraction and processing of tar sands). In addition to the hydrocarbon component, crude oil may contain trace amounts of compounds containing sulphur, nitrogen, oxygen, and heavy metals such as iron, nickel, chromium and vanadium.

The Ministry of the Environment has carried out an economic profile of this sector (13), in order to provide background information for future economic assessment, as part of the effluent limits setting process.

Products

While not all refineries necessarily make a full range of products, generally speaking, refineries transform crude oil into about 700 products including greases, waxes, asphalts, lubricating oils, several grades of gasoline, many grades and types of fuel oils, (i.e. diesel, home heating, industrial and heavy fuel oils) and petrochemicals.

The primary petrochemical producer can utilize a wide range of feedstocks in addition to crude oil, including natural gas liquids (NGLs - ethane, propane, and butane), and vacuum gas oil (VGO). The choice depends upon the product requirements and the price and availability of the raw materials.

The primary petrochemicals produced are ethylene, propylene, butadiene, butylenes, benzene, toluene, and xylene. Coincident with petrochemical production, some fuel co-products result, including synthetic natural gas, liquified petroleum gas, gasoline components, diesel fuel, home heating oil, and heavy residual fuel oil.

Refinery Processes

The basic function of a refinery is to process crude oils into the variety of petroleum products required by an industrialized society. Moreover, it is important to note that a typical refinery produces petrochemical feedstocks that are the raw materials for a myriad of products manufactured by other industries.

The first process step in a refinery consists of physically separating crude oil into a number of fractions of varying molecular weights by distillation. Subsequent conversion processes are then required for intermediate and final products. Although more than 150 separate processes have been identified in the industry, they can generally be classified as either physical separation or chemical conversion operations.

Distillation, liquid extraction and crystallization are examples of common physical separation processes. Cracking, reforming and alkylation are examples of the major chemical conversion processes used. Finished products are manufactured by blending various intermediate products in the required proportions. Additives, such as anti-oxidants, anti-icing agents, corrosion inhibitors, and anti-knock agents, are added at this stage.

Wastewater Sources

A refinery generates contaminated water in a number of ways:

- crude oil itself contains a small amount of water;
- steam is added in the processing operations to aid in the distillation or to 'strip' out impurities;
- ballast water from tank ships transporting petroleum products is pumped ashore when products are loaded;
- water accumulates in the bottom of storage tanks and must be drawn off from time to time;
- periodic discharge, or blowdown, of recirculating cooling water systems;
- stormwater runoff from process areas and tank farms.

The Makeup and Treatment of Petroleum Refining Industry Liquid Effluents

In the past, sulphides, ammonia, and oil and grease were significant pollutants from the refineries. pH and sulphides are still reported under the federal Refinery Guidelines noted below; the major traditional pollutants federally regulated in Canada and in the United States are the parameters described below.

In Ontario, petroleum refineries report five parameters which are considered representative of their effluents; these parameters are:

- phenolics ("Reactive Phenols" measured by the 4-amino-antipyrine method);
- ammonia-nitrogen;
- total suspended solids;
- oil and grease;
- acute toxicity to fish as measured by a 24-hour static test.

The parameters described above along with sulphides and substances capable of altering pH are designated as 'deleterious substances' in wastewater from the petroleum refining industry under the federal Fisheries Act. The general prohibition under the act forbids the deposition of 'deleterious substances' in 'water frequented by fish'.

Section 33 of the Act empowers the federal Environment Minister to impose regulations or guidelines designating effluent components as deleterious substances which may then only be discharged at authorized levels.

Guidelines, for older refineries, and regulations, for new refineries (14), were brought into force in 1973. Under the Canada-Ontario Accord (15), Ontario applies these regulations and guidelines.

Two acute toxicity fish tests are applied under Guidelines for both existing refineries and new refineries which began operations after October, 1973. The 24-hour routine test -- formally called the Twenty-Four Hour Static Bioassay Procedure -- is performed as noted above and reported to federal and provincial agencies. Some refineries may already apply the Ontario test as differentiated below.

The 'governing' toxicity test -- the Ninety-Six Hour Flow Through Bioassay Procedure -- is conducted periodically by government agencies to determine acceptability of the effluents. In practice, most regulatory agencies carry out a static procedure which is considered approximately equivalent.

The federal tests differ significantly from the Ministry of the Environment tests in that the federal tests are single concentration pass-fail tests, although both tests use rainbow trout. The federal tests also allow the combination of samples proportional to flow and the dilution of the undiluted 'bioassay sample' with uncontaminated water calculated from water use figures at each refinery.

Mortality greater than 6% on the control water (which may be intake water) invalidates the test.

Wastewater Treatment

The aim of the federal Regulations and Guidelines for the petroleum refining industry was to ensure that all refineries operating in Canada would apply best practicable treatment technology (BPT) to their liquid effluents.

For the purpose of the Regulations and Guidelines this means a system equivalent to the following:

- Primary separation (such as an American Petroleum Institute (API) separator described below):

  Oil removal from wastewater is achieved by gravity separation. The most commonly found separators are specially designed long, rectangular basins (API Separators). Other more recent designs incorporate tilted plates to increase the surface area for the oil to coalesce more rapidly (eg. corrugated plate interceptors or tilted plate interceptors). The oil which rises to the surface is removed by skimming devices and returned to the refinery for reprocessing;

- Intermediate treatment (such as the air flotation described below):

  Any traces of oil in the effluent from the separator can be further decreased with such processes as dissolved air flotation, induced air flotation, and filtration with sand or mixed media, as required.

- Secondary treatment (the biological oxidation described below):

  Wastewater from all of the primary containment and treatment steps is collected in a feed equalization pond to smooth out the quality and quantity of the feed to the "Secondary" treatment stage, the biological oxidation unit. These retention ponds typically provide anywhere from 12 hours to several days hold-up time.

  The wastewater is fed into an aerated basin which contains bacteria which have been conditioned to consume the organic contaminants remaining in the wastewater. The biological activity produces new cell matter (to propagate the species), carbon dioxide, and water.

  A final clarification or effluent polishing step removes any biological floc or other suspended matter. It also adds further hold-up and equalization in the system before the treated wastewater is discharged to the receiving water;

- Sour water stripping for ammonia and sulphide removal:

  Certain of the wastewater streams contain appreciable quantities of ammonia and sulphides. These are removed in a steam stripping column, called a sour water stripper, prior to further treatment using the system as outlined above.

- Good housekeeping, such as sewer segregation:

  The sewer systems in which on-site wastewater is collected and transferred to the wastewater treatment plant are designed to keep the various types and strengths of wastewaters separate in order to facilitate more efficient and effective treatment. An example of this is the segregation of sour waters for stripping mentioned above.

Stormwater

Stormwater falling on the developed areas of a refinery site is collected in large retention ponds. The ponds are subsequently tested and either discharged or treated, depending upon the quality.

It should be noted that all petroleum refining treatment systems used in Ontario have received Certificates of Approval under the Ontario Water Resources Act prior to operation.

APPENDIX A - DESCRIPTION OF PETROLEUM REFINERIES IN ONTARIO

SUNCOR SARNIA REFINERY

The Suncor Sarnia refinery was built in 1953. The refinery is located on the St. Clair River immediately adjacent to, and downstream from, the major Sarnia petrochemical complexes.

During 1987, approximately 9,000 cubic meters per day of crude oil were processed into motor gasolines, light and heavy fuels, light aromatic products, liquified gases and solid sulphur.

The refinery processes include atmospheric and vacuum distillation, catalytic cracking, hydrocracking, catalytic reforming, and BTX (benzene, toluene, xylene) aromatic extraction, as well as various strippers, hydrotreaters and scrubbers.

All gas streams containing hydrogen sulfide (H_2S) are collected and approximately 24 metric tonnes per day of elemental sulphur are recovered in a Claus sulphur unit.

All wastewater from condensates, contaminated storm collection systems and ballast water is treated for removal and recovery of oil. The wastewater is biologically treated before discharging to the St. Clair River through a single discharge point. Approximately 10,000 cubic metres of effluent are discharged daily together with 100,000 cubic metres of once-through cooling water.

PETRO-CANADA TRAFALGAR REFINERY

Petro-Canada's Trafalgar Refinery is located in the Town of Oakville, Ontario. It was commissioned in the Fall of 1958. The past 30 years have seen a greater than fourfold increase in the refinery. At present, the refinery can process a maximum of 13,600 cubic metres of crude oil per day. Trafalgar refinery's product slate covers virtually the entire range of petroleum fuel products - liquid petroleum gases, aviation gasoline, motor gasolines, distillates, residual fuel oils, asphalt and sulphur.

The wastewater effluent treatment system consists of sour water strippers, an API oil separator, feed equalization, induced air flotation and biological oxidation units. An odour control system has been installed for the induced air flotation and biological oxidation units to remove odorous gases.

Stormwater is sent to an API oil separator and, depending upon the concentration of contaminants, can be treated along with the process wastewater. Trafalgar Refinery has a recirculating cooling water tower system. The combined effluent consists of process wastewater, stormwater, and cooling tower blowdown, and is discharged to Lake Ontario via the surge lagoon.

PETRO-CANADA CLARKSON REFINERY

Petro-Canada's Clarkson facility is situated in Mississauga, Ontario. It was opened in 1943 by the British American Oil Company. The facility encompasses a refinery and lubricants plant including a compounding, blending, and grease plant. In response to a decline in market demand, the refining portion of the facilities was downsized in 1984. It can now process up to 7,100 cubic meters per day of Canadian crude oil into a variety of products, including liquid petroleum gases, aviation fuel, motor gasolines, distillates, residual fuel oils, asphalt, lubricating oils and greases, and solvents.

The Clarkson operation has a modern wastewater effluent treatment plant. The effluent plant consists of a sour water stripper, an API oil separator, sand filter, feed equalization, and biological oxidation unit. It treats both process effluents and stormwater. As in most older, large refineries, significant quantities of water are used for cooling in the process units. Once-through cooling water is sent to an API oil separator prior to discharge into Lake Ontario.

SARNIA MANUFACTURING CENTRE, SHELL CANADA PRODUCTS LIMITED

Shell's Sarnia Manufacturing Centre (SMC) is located on the St. Clair River south of Sarnia, at Corunna, Ontario. It comprises an oil refinery built in 1952 and a chemical plant built in 1979. Combined employment is about 530.

The Refinery has a crude capacity of 11,800 cubic meters per day. In addition to gasoline, diesel, furnace fuel and bunker fuel, the product slate includes pure chemicals (benzene, toluene, xylene, and sulphur) as well as hydrocarbon solvents.

The chemical plant is made up of two facilities, one for manufacturing polypropylene, the other for manufacturing isopropyl alcohol. The capacity of the isopropyl alcohol plant is 91,000 tonnes/year and the capacity of the polypropylene plant is 80,000 tonnes/year. All of the wastewater is treated in the wastewater treatment facility.

SMC takes about 200,000 to 300,000 cubic metres of water from the St. Clair River each day. The largest portion (100,000 to 200,000 cubic metres) of this water is once-through cooling water. It is used in coolers where the water pressure is higher than the product pressure, and so it is not normally contaminated. The remainder is either contaminated, or potentially contaminated, and treatment is provided.

Treatment is also provided for stormwater collected in a system of in-plant ditches. In April 1988, a new 30,000 cubic metre stormwater retention pond will be commissioned to further enhance the capability to collect and treat stormwater.

Ballast water from ships is pumped ashore and treated in the on-site wastewater treatment facility.

The wastewater treatment facility consists of API oil/water separators, dissolved air flotation, sour water stripping, flow equalization, biological oxidation, and clarification.

TEXACO NANTICOKE REFINERY

The Texaco Nanticoke refinery is located south-west of Hamilton on the north shore of Lake Erie. It was completed in 1978 with a crude oil processing capacity of 15,200 cubic meters per day. The refinery utilizes atmospheric and vacuum distillation, fluid catalytic cracking, catalytic reforming, alkylation, and sulphur recovery processes. Finished products include leaded and unleaded gasolines, jet fuels, heating oils, diesel, industrial fuels, liquified propane and butane, and sulphur.

Approximately 85% of the refinery's cooling requirements are fulfilled by air rather than water. Water usage is minimized by recirculating the water through a cooling tower and by re-use of process waters and steam condensate.

Pre-treatment at the source, by sour water stripping or spent caustic neutralization, is provided for certain wastes. Other waste streams that are segregated include: process wastewaters, ballast water, clean stormwater, sanitary wastes, cooling tower blowdown and other high dissolved solids containing streams and oil wastes. All waste streams are directed to the wastewater treatment plant for final processing before discharging to Lake Erie.

Wastewater is treated sequentially through API separators, feed equalization, dissolved air flotation, biological activated sludge, secondary clarifiers, polishing filters, and final effluent containment ponds. The wastewater treatment plant also has a containment pond to allow the recycle of waste streams being treated.

Uncontaminated stormwater has a segregated sewer/ditch system leading to a modified API separator before being collected in two clean storm containment ponds. The effluents from these ponds are analyzed prior to discharge and can be routed to the wastewater treatment plant if necessary.

ESSO PETROLEUM SARNIA REFINERY

The Esso Petroleum refinery in Sarnia is nearly 90 years old. It has a crude oil capacity of 20,000 cubic meters per day. It is a very complex combination of fuel products, packaging, lubricating oil, and petrochemical operations. Major processes include: atmospheric and vacuum distillation, catalytic cracking, fluid coking, hydrocracking, catalytic reforming, alkylation, polymerization, hydrogen treating, naphtha and gas oil aromatics extraction, dewaxing, and thermal cracking.

The refinery has segregated systems for treating once-through cooling water and oil contact water.

Once-through cooling water is treated in four parallel API separators for solids and oil removal prior to discharge.

Oil contact water consists of process wastewater, stormwater, ship's ballast, tank water draw-off, and landfarm leachate. The wastewater treatment sequence is comprised of API oil/water separation, sand/anthracite filtration, biological oxidation, and clarification.

Sour water is steam stripped to remove sulphides and ammonia and then transferred to a biological oxidation unit. The effluent is then combined with the filtered oil contact water and transferred to another biological oxidation unit.

Stormwater storage tankage is provided, which is sufficient to contain the runoff from a one in 10 year storm event, in order to prevent the overloading of the treatment facilities.

An active source control program quickly identifies and corrects leaks or other problems before they can adversely affect the operation of the treatment plant.

PETROSAR LIMITED

Petrosar Limited's petrochemical refinery complex commenced operation in 1978. It processes crude oil, condensate, and natural gas liquids for the production of 1.3 million tonnes per year of primary petrochemicals (ethylene, propylene, butadiene, iso-butylene, n-butylene, benzene, and toluene/xylene).

Naphtha, heavy atmospheric gas oil, vacuum gas oil, No. 2 fuel oil, ethane, propane, and butane are all produced as intermediate or final products. Whether they are further processed (i.e. cracked) or solid depends upon market demand and economics.

The main processes in the complex are atmospheric and vacuum distillation, olefin cracking and separation, gasoline hydrotreating, and aromatics extraction.

The wastewater is segregated into four types: chemical or process wastewater, oily water, stormwater, and sanitary wastewater.

All chemically or oily contaminated water is treated in a tertiary treatment plant consisting of oil/water separation, retention pond, biological oxidation, and activated carbon filtration. Stormwater is treated to remove suspended solids and traces of oil. Sanitary wastewater is treated in a separate biological unit.

DEVELOPMENT OF THE EFFLUENT MONITORING REGULATION FOR THE PETROLEUM REFINING SECTOR

THE PETROLEUM REFINING SECTOR MONITORING REGULATION

The Effluent Monitoring Regulation for the Petroleum Refining Sector is designed to provide an accurate and credible status report for priority and traditional pollutants from this industry and to identify any residual problems for the development of further controls.

The regulation was developed by the Ministry in consultation with representatives from the petroleum refining industry and Environment Canada through the Joint Technical Committee (JTC) for the Petroleum Refinery Sector. The MISA Advisory Committee provided meaningful input to the regulation.

As part of the pre-regulation program, a working group of the JTC reviewed an extensive list of studies concerning trace contaminants in treated oil refinery wastewaters. A detailed discussion of these reports, along with the working group's recommendations, is provided in Appendix B. Generally, these studies indicated that there were no major immediate concerns with respect to the impact of the treated refinery effluents on receiving waters. However, the studies did indicate that there is the potential for the discharge of a number of substances at levels which may be environmentally significant.

It was therefore determined that the appropriate monitoring approach was one that would assess the loadings and the frequency and magnitude of losses of those substances most likely to be discharged from the petroleum refining sector under everyday operating conditions. The variability of effluents would be statistically established by analytical methods in a framework of quality assurance and quality control. Intake waters, if considered important contributors of contaminants, could be monitored voluntarily by the discharger to aid in the analysis. The literature study also revealed the need for further research to develop detection levels for specific analytes within analytical groups. The Ministry will carry out this research on alkylated polynuclear aromatic hydrocarbons (PAHs), and other groups of concern such as mercaptans, thiophenes, ketones and alkylated phenolics.

Specific analytes that are detected will be assessed using the Hazard Assessment Screen and added to EMPPL as warranted. The Ministry will then develop analytical methods necessary to quantify the analytes added to EMPPL.

A review of biological studies (see Appendix B) also indicated that there are discharges of potentially toxic substances. These substances are discharged at levels which can only be assessed by the introduction of methods such as Daphnia magna testing -- a testing process that, according to reports published by the Petroleum Association for Conservation of the Canadian Environment (PACE), is sensitive and predictive. Daphnia magna tests have therefore been included in the monitoring regulation. The concerns about potential carcinogens raised in one of these studies will only be resolved by research focussed on the speciation and evaluation of the toxic components of refinery effluents, in particular the polynuclear aromatic hydrocarbons.

The specific requirements of the Effluent Monitoring Regulation for the Petroleum Refining Sector are provided below.

MONITORING FREQUENCIES

The regulation specifies several monitoring frequencies and the compounds to be monitored at each frequency for process effluent: daily - three parameters; three times weekly - 16 parameters; quarterly - 109 parameters; two characterizations in the first year - 148 parameters. The process effluent sampling points selected are those upstream from the point of discharge to a surface watercourse, downstream from final treatment and upstream of dilution with once-through cooling water or any other form of contaminant masking. No combined effluents are to be sampled since separate process effluents and cooling water sampling sites were available.

Cooling waters, emergency overflows, stormwater runoff, and landfarm leachate must also be monitored. Toxicity tests are required each month for process effluent, and quarterly for cooling water effluents.

Detailed descriptions of these requirements are presented below.

The Characterization Monitoring List

The annual characterization monitoring list (sector specific list) for the petroleum refining sector includes a total of 148 compounds consisting of traditional pollutants and a subset of the EMPPL. All other monitoring at different frequencies is conducted on contaminants from this sector list.

Those compounds on EMPPL but not on the sector list were eliminated for one of the following reasons; the compounds:

- were not reported present in the research studies reviewed, nor were they detected by the open-ended scans conducted by the Ministry, nor are they likely to arise from refinery operations; for example, resin and fatty acids which are associated with pulp and paper effluents have no association with petroleum refinery effluents;

- cannot be monitored currently because analytical protocols are not available -- when these are developed the compounds may be added to the sector list, if appropriate.

Dischargers are required to undertake characterization for the complete sector list within three months of the first routine sampling, once between four and seven months later, every three years thereafter and following each process change which could adversely affect effluent quality. Characterization of refinery process effluents is not required after experimental process changes of less than 30 days duration.

As part of its sampling program, the Ministry will continue to conduct open-ended characterization studies as described earlier in "Approach".

The approach agreed to with the Ontario Petroleum Association does not require the refineries to carry out open characterizations for the following reasons:

- the Ontario Petroleum Association provided substantial amounts of data on contaminants in refinery effluents to the Ministry (as noted elsewhere);
- refinery effluents are essentially similar due to similarities in processes and raw materials;
- previous characterization studies identified several contaminants falling into groups which needed further research to speciate and confirm the presence of, for example, little known methylated PAHs;
- prior studies generally indicated that refinery wastewaters in Ontario receive adequate treatment;
- the Ministry recognized that the identification of additional contaminants in refinery effluents required Ministry attention as part of an audit program, thus assuring credibility and follow-up.

Daily Chemical Monitoring For Process Effluents

The parameters chosen for daily monitoring are indicator parameters, which monitor treatment process effectiveness. These indicators provide a cost-effective assessment of treatment system effectiveness and hence gross effluent quality.

Petroleum refineries will monitor daily for phenolics (4AAP), volatile suspended solids, and pH. The rationale for including these parameters is provided below:

Phenolics

- recommended in the literature as the single best measure of petroleum refinery effluent treatment;
- US EPA limit in regulations for the petroleum refining sector;
- currently monitored frequently at refineries;
- limited and required to be monitored three times per week under the Fisheries Act Regulations and Guidelines;
- recommended for daily monitoring by JTC Trace Contaminants Working Group.

Volatile Suspended Solids

- provides a measure of the organic biological floc associated with biological treatment systems;
- measures treatment plant effectiveness in removing organic solids in the final sedimentation process;
- a component of total suspended solids.

pH

- a measure of acidic or caustic level in the wastes; intended to pick up excess discharges of caustics or alkalis used in the process;
- US EPA limit in regulations;
- currently monitored daily;
- indirectly limited and monitored seven times per week under the Fisheries Act.

Three Times Per Week Chemical Monitoring for Process Effluents

The parameters chosen for thrice weekly monitoring are usually present in untreated process wastewater from petroleum refineries and are of potential environmental significance.

Petroleum refineries will monitor thrice weekly for both toxic and traditional pollutants. The toxic contaminants are benzene, toluene, o-xylene, m-xylene and p-xylene (measured together), ethylbenzene, chromium, and zinc. Chromium and zinc will be monitored only at refineries that use these metals in the treatment of cooling water.

The traditional pollutants are ammonia nitrogen, total and dissolved organic carbon, total phosphorus, total suspended solids, sulphide, and oil and grease.

The rationale for including these traditional and toxic contaminants on the thrice weekly monitoring list is provided below.

Ammonia plus ammonium nitrogen	■ a measure of the dissolved ammonium originating from sour water wastewaters;
	■ ammonia (un-ionized) is toxic to fish at low levels; toxicity varies with pH;
	■ US EPA limit in regulations;
	■ Fisheries Act limit on ammonia;
	■ currently monitored three times per week as required under the Fisheries Act Guidelines and Regulations.
Total organic carbon	■ a gross measure of the total organic carbon content, both particulate and dissolved -- crude oil and petroleum products, primarily hydrocarbons, are measured in this test.
	■ an indicator of treatment efficiency -- the carbon associated with biological floc is also measured;
	■ currently measured three times per week as a treatment process variable;
	■ current technology is not capable of measuring this at low levels; consequently, dischargers are not required to analyze for this when total suspended solids are below 15 mg/l.
Dissolved organic carbon	■ the soluble portion of organic carbon as a component of the above parameter -- related to the soluble portion of crude oil and petroleum products;

	■ much lower detection limit than total organic carbon and hence more likely to be comparable to dissolved trace organic contaminants at low levels.
Total suspended solids (TSS)	■ gross measure of suspended material including biological flocs associated with the treatment process -- includes volatile suspended solids, the concentration of which is measured daily; ■ good measure of effectiveness of the treatment system in removing solids; ■ toxic contaminants may be associated with particulate matter; ■ US EPA limit in regulations; ■ limited and monitored three times per week under the Fisheries Act.
Sulphides	■ a contaminant in crude oil associated with sour water as hydrogen sulphide and other reduced sulphur species; ■ US EPA limits in regulations; ■ limited and monitored three times per week under the Fisheries Act.
Total phosphorus	■ added to petroleum refinery treatment systems as a nutrient to aid in biological growth; ■ phosphorus discharges to the Great Lakes are identified as a concern in the Canada-United States Great Lakes Water Quality Agreement; ■ indicates to the operator if too much or too little phosphorus has been added to the treatment system.
Oil and Grease	■ a measure of gross visible pollution from petroleum materials including oil sheens on surface water; ■ associated with other contaminants in crude oil and products; ■ US EPA limits in regulation;

- limited and monitored three times per week under the Fisheries Act;

The petroleum refineries are also required to monitor for the following organic contaminants and metals:

Benzene, ethylbenzene, toluene, xylenes (o-xylene, m-xylene and p-xylene)

- aromatic hydrocarbons produced as petrochemical feedstock;
- present at high concentrations in intermediate wastewater;
- historically detected in final effluents;
- all contaminants, with the exception of ethylbenzene, are listed on EMPPL;
- all recommended by JTC working group as demonstration parameters i.e., to demonstrate the treatment performance for toxic removal;
- with the exception of xylenes, all are US EPA priority pollutants.

Chromium and Zinc

- monitoring is only required at this frequency where these contaminants are used as corrosion inhibitors;
- often detected at high levels in intermediate wastewaters and frequently detected in effluents;
- both contaminants are listed on EMPPL.

Quarterly Monitoring For Process Effluents

The same sampling effort as monthly - 12 times per year - has been provided for in quarterly "cluster" sampling in the petroleum refining sector.

Monitoring will require clusters of three daily samples to be taken during a single week, four times per year. This has the advantage of providing more than one result in a short time-span for each parameter in each season. The logistics of sampling, transportation and laboratory analysis are simplified, potentially reducing the cost where contract laboratories are used.

Quarterly monitoring for a cluster of three samples in a week each quarter provides a good estimate of process variations over a short time period. It should only be used when a high level of treatment already exists, sufficient historical characterization data are available, and process variations do not cause large differences in waste characteristics. Monthly monitoring provides a statistically independent check on the presence or absence of contaminants, and, thus, is preferred when variations are expected based upon process cycles, and where historical characterization data is inadequate.

Parameters have been chosen for quarterly monitoring because they are known to be present or are likely to be present in petroleum refinery effluent. Those present have usually been detected at low concentrations in final effluents, but have been detected frequently in significant concentrations in wastes prior to biological treatment. The concentrations in final effluents may therefore fluctuate and be environmentally significant over the long term.

The purpose of quarterly monitoring is to establish a data base for twenty groups of pollutants from the sector specific list. The rationale for the quarterly monitoring list is provided below.

Chemical Oxygen Demand (COD)	■ a measure of total oxygen demanding material including organic material and refractory (non-biodegradable) compounds. Biochemical oxygen demand was also considered, but eliminated because of analytical problems - i.e., laboratories carrying out this test must maintain an acclimated bacterial seed for each industrial effluent; ■ US EPA limit in regulations; ■ other parameters monitored more frequently, such as TOC, DOC, and VSS, provide similar information;
Cyanide	■ toxic substance frequently in intermediate treated wastewaters, and occasionally in effluents; ■ listed on EMPPL.
Specific conductance	■ indicator of the presence of inorganic salts which are contaminants in crude oil; ■ indicator of the range of loadings from the processes that generate this waste;

	■ monitored at a relatively low frequency because it is not of great concern to the environment at the levels expected in this sector.
Hexavalent chromium	■ most toxic form of chromium;
	■ required to be analyzed only if total chromium is above a certain (trigger) concentration (i.e. 1.0 mg/L);
	■ monitored at this frequency in conjunction with the metal scan;
Total metals	■ scan for 13 metals on EMPPL including chromium and zinc;
	■ many metals occasionally or rarely detected at levels of concern in effluents and intermediate wastewater;
	■ not necessarily removed efficiently by biological treatment.
Total alkyl lead	■ used as a gasoline additive, which may be used at the refinery in blending operations;
	■ analyzed only when total lead is detected above 1.0 mg/L in the metal scan.
Hydrides (antimony, arsenic, selenium)	
	■ similar in occurrences to metals;
	■ listed on EMPPL.
Mercury	■ rarely detected in intermediate wastewaters and/or effluents;
	■ listed on EMPPL.
Nitrogen (all forms including ammonia and ammonium, total Kjeldahl, and nitrite plus nitrate)	
	■ these nitrogen compounds are used as a check on nitrogen transformations caused by biological activity to provide additional information describing the biological activity of the treatment system;
	■ measurement of nitrification efficiency;

	■ check on the hypothesis that treatment plants which foster nitrification provide higher levels of organic toxic contaminant removal.
Volatiles, halogenated	■ compounds from this group have been historically detected in refinery effluent; earlier studies, however, could not identify their source i.e., whether these compounds originate from intake water, or chlorine additions to cooling water, or whether these have been detected because they are prevalent in the laboratory environment; ■ listed on EMPPL; ■ companies have the option of monitoring these parameters in intake waters, in conjunction with quarterly sampling, to aid in determining the sources.
Volatiles, non-halogenated	■ all compounds in this group which are on EMPPL are monitored more frequently except for styrene: styrene has not been detected in petroleum effluents.
Volatiles, water soluble	■ two substances from this group are on EMPPL. ■ new evidence indicates the potential presence of acrolein, which is a water soluble volatile compound, in refinery effluents.
Extractables, base neutral	■ a large group of compounds on EMPPL, including 22 compounds which are polynuclear aromatic hydrocarbons (PAHs); ■ little is known about the PAHs, particularly alkylated PAHs which have been identified as potentially carcinogenic and hence of environmental concern: further research to develop additional analytical methodologies for identification and quantification of these alkylated compounds is needed -- a subsequent hazard assessment will then determine the need to include these contaminants on EMPPL; ■ phthalate compounds were not included even though they have been reported in refinery effluent samples. Available data in the literature indicates that the detection of

	phthalates at low levels in refinery effluent samples is most likely an artifact of the sampling and analytical methodology. Many analyses of refinery intake and effluent samples in the current data base have not shown any consistent difference which would dispute this conclusion. (References: "Evaluation of the Variability of Trace Organic Substances in Petroleum Refinery Effluents"(16); "Sampling and Analysis of Refinery Effluents to Assess Variations in Trace Contaminant Concentrations"(17)).
	■ Other compounds from this group were not included on the quarterly monitoring program because they were not detected or expected from refinery processes.
Extractables, acid	■ phenolic and chlorinated phenolic compounds are on EMPPL; ■ some members of this group have been detected occasionally in effluent.

Chemicals from the analytical test groups 23 (Extractables, neutral chlorinated); 24 (Dioxins and Furans); 26 (Fatty and Resin Acids); and 27 (PCBs) were not included under quarterly monitoring. These chemicals are not expected from refinery processes and with the exception of hexachlorobenzene (HCB) have not been reported in effluents. HCB from group 23 was reported at levels marginally above the detection limit; however, it was also present at the same levels in intake waters. These groups will be monitored by the refineries as part of characterization and by the Ministry as part of the audit program.

Cooling Water Monitoring

In this sector, once through cooling water streams will be monitored each month for the following parameters: pH, total and dissolved organic carbon, total and volatile suspended solids, phenolics (4AAP), sulphide, benzene, toluene, o-xylene, m-xylene and p-xylene, ethylbenzene, and oil and grease.

This is the same list as is used for the three times weekly monitoring for process effluents, excluding total phosphorus and ammonia (plus ammonium) nitrogen. The parameters on the list are primarily indicators, gross measures, or actual measures of crude oil, wastes, or petroleum products.

The monthly frequency will identify minor continuous leaks from processing areas into cooling waters. Phosphorus and nitrogen are not included since they are measures of the biological activity in the treatment system and not of process wastes directly. Chromium and zinc are also required to be monitored, if these are added to cooling waters.

It is also required, in the reporting section of the regulations, that reports on addition of chemicals to cooling waters be provided. An initial report is required on chemicals added to cooling waters such as slimicides, algicides, or anti-corrosives based on usage in the previous calendar year. Actual usage must be reported on a quarterly basis within the regulation. This information will be used to estimate loadings, to provide input to a hazard assessment, and for consideration for adding these chemicals to EMPPL.

Event Monitoring For Stormwater, Emergency Overflows and Landfarm Leachate

The comprehensive collection systems present at refinery sites allows all contaminated and potentially contaminated stormwater to be retained and treated most of the time. Therefore, monitoring of stormwater is required only when it is discharged to the environment.

Stormwater discharged from refinery sites will be monitored for the following parameters: pH, ammonia (plus ammonium) nitrogen, dissolved organic carbon, total phosphorus, total and volatile suspended solids, chromium and zinc (where used), phenolics (4AAP), sulphide, benzene, toluene, o-xylene, m-xylene and p-xylene, ethylbenzene, and oil and grease.

This list is the same as the thrice weekly monitoring list. This will indicate if any raw materials or products have been lost, as well as ammonia or phosphorus which may be present in runoff.

When untreated or incompletely treated process effluent overflows, the emergency overflow streams will also be monitored for the same compounds as the thrice weekly monitoring list.

Landfarm leachate, which can also be retained and treated at refinery sites, will be monitored for the three times weekly list when discharged to the environment and for the quarterly list at least once per year.

Many leachate discharges to surface waters are currently subject to monitoring conditions on Certificates of Approval under Part V of the Environmental Protection Act.

TOXICITY TESTING

Two toxicity tests are in the petroleum refining regulation: the Rainbow Trout Acute Lethality Test, and the _Daphnia_ _magna_ Acute Lethality test.

The Rainbow Trout Acute Lethality Test will be conducted on effluent that has been treated but has not been diluted by cooling water or other waste streams. This is a more stringent application than in the past for the similar acute toxicity test carried out under the federal Fisheries Act.

The OPA agreed to this measure in recognition of the MISA goal of virtual elimination. In the past, refineries have tested final effluent and usually found no acute lethal effects. Now, by testing undiluted effluent, they are moving a step closer to the MISA goal.

Testing at this point will also provide information on the performance of on-site treatment facilities.

The tests will be carried out monthly on process effluents. If a process effluent passes the acute lethality test (i.e., no more than two out of ten fish die in a test) for three consecutive tests, then the frequency of sampling for that effluent will be reduced to once per quarter, in recognition of the extensive data set from these sites showing no acute toxicity.

The _Daphnia_ _magna_ test, on the other hand, will be continued at the higher frequency since less information is available on this test, which has not been routinely applied to these effluents in the past.

Once-through cooling water will be subjected to both tests once each quarter using both trout and _Daphnia_. The impact of leaks and the use of algicides and slimicides will be checked.

The regulation also requires that chemical sampling take place on the same day as the sampling for toxicity testing.

ECONOMIC IMPLICATIONS OF THE MONITORING REGULATION

Separate estimates of the incremental capital and operating costs to Ontario refineries in complying with the monitoring regulations have been prepared by the Ontario Petroleum Association and staff at the Ministry of the Environment. These estimates will be described and summarized in the report, "Cost Estimates and Implications of the Petroleum Refinery Effluent Monitoring Regulation for Ontario's Petroleum Refineries"(18).

The OPA estimated that the capital costs would total $1.7 million for all seven refineries. The MOE estimates indicate that the regulation requirements could be implemented for a minimum capital cost of $700,000.

The OPA expects operating costs to total $2.3 million during the 18-month term of the regulations for all refineries. The MOE estimated these costs to total $1.9 million.

The cost estimates from either source are not definitive but only indicate the range of potential costs that would be imposed by the regulations.

The petroleum refining industry has contracted in recent years due to closures and slow growth in product demand. Long term growth and return on investment is expected to be modest at best.

These monitoring requirements have been developed in recognition of a concern for collecting a comprehensive data base in a cost-effective manner. Through on-going consultation, the Ministry and industry will continue to strive for cost-effective requirements.

APPENDIX B - APPROACHES TO THE MONITORING OF PETROLEUM REFINING WASTES

APPROACHES TO THE MONITORING OF PETROLEUM REFINERY WASTES

Background

Through the efforts of the Ontario Petroleum Association (OPA), the Petroleum Association for Conservation of the Canadian Environment (PACE) and Environment Canada, there is a significant quantity of historical and current monitoring data available from short term studies which were used to assist in the development of the monitoring regulation. While the short term studies have been essential to the development of practical regulations, the data were not sufficient to achieve the objective of the Effluent Monitoring Regulation.

Other industrial sectors in Ontario have not placed in the public domain equivalent studies on the priority pollutants in their effluents. They may be required to supply more information on their effluents during the pre-regulatory phase and to do more monitoring under regulation. The monitoring regulation for this industrial sector will, however, provide the framework on which to base the regulations for other industrial sectors.

PREVIOUS STUDIES

Chemical Monitoring

A PACE report entitled "Survey of Liquid Effluent Discharges From Canadian Petroleum Refineries"(19), reported the results of a 1980 survey on the nature and effectiveness of the wastewater treatment systems in place. Thirty-two Canadian refineries reported comparisons between 1972 data and 1980 status, seven years after the implementation of the Petroleum Refining Effluent Regulations and Guidelines under the Fisheries Act.

Summary statements for the national scenario, relevant to the development of the Monitoring Regulation for the Petroleum Refining Sector, were as follows:

- Water use: a national decrease in 'relative flowrate' (factoring in discrepancies from differences in reporting of stormwater between 1972 and 1980) of 50%. Actual flowrate based on monthly averages showed a reduction of 44.5%.
- Stormwater: 30% of effluent was noted to be stormwater. By and large this water was segregated, managed and could be treated prior to discharge. Retention ponds were present at 13 refineries to reduce shock-loadings to the secondary treatment systems.
- Net/gross considerations: intake water was not universally monitored. Fifteen Sarnia and Montreal refineries noted the need to define intake water polluted by upstream sources and potentially claim net credits for the parameters controlled under the Fisheries Act.

Four PACE studies, conducted between 1980 and 1984, were designed using experience gained and data produced from studies by the American Petroleum Institute (API) in the United States. US EPA analytical methods were generally used to determine the presence, absence and concentrations of a subset of the US EPA Priority Pollutants (the list of 126 'Consent Decree' pollutants) in selected Canadian refinery effluents.

The report entitled "Survey of Trace Substances in Canadian Petroleum Industry Effluents"(20), noted:

> "On the basis of the findings in the API report and consideration of Canadian legislation, a list of 58 parameters was defined for further study in this Canadian survey of seven refining operations."

The same report noted further that:

> "A number of organic compounds derived from crude oil or from individual process units were detected in the intermediate treatment waters, but concentrations were generally lower in corresponding final effluent samples.
>
> Substances frequently detected in the refinery effluents included benzene, toluene, ethylbenzene, phenol, poly-aromatic hydrocarbons, iron, chromium, ammonia nitrogen and fluoride. The significance of the findings has not been fully assessed at this stage, although fluoride appears to be related to operation of HF alkylation units and benzene, ethylbenzene and toluene to aromatic units. Many of the parameters detected are not normally regulated in discharge permits. Twenty-one of the list of fifty-eight substances were not detected in any of the effluent samples collected and others were detected at very low concentrations."

A PACE report entitled "Comprehensive Characterization of Organic Substances in Petroleum Refinery Wastewaters"(21), defined a specific list of target compounds based on the report cited above for 'comprehensive characterization' and also identified additional compounds through Gas Chromatography/Mass Spectrometry - (Open Characterization).

Forty-six samples of water and wastewater from seven Canadian refineries were analyzed in total, focussing on the 58 specific trace compounds selected on the basis of U.S. studies and confirmed in the earlier PACE study. Qualitative analyses were carried out to confirm the tentative identification of other organic compounds.

This report confirmed once more that both intermediate treatment waters and final effluents contained benzene, toluene, ethylbenzene, phenol and low concentrations of polynuclear aromatic hydrocarbons. The report noted further that the predominant species, confirming previous studies, were benzene, at concentrations of up to 160 ug/L in final effluent, and substituted benzenes, at concentrations of up to 780 ug/L in final effluent and up to 71,000 ug/L in intermediate treatment effluent. Naphthalene, substituted naphthalenes and polynuclear aromatic hydrocarbons, mainly phenanthrenes, and phenols were also prevalent at widely ranging concentrations, always much higher in intermediate treatment waters than in final effluents.

The report recommended that the major substances be routinely quantified using GC/MS target analyses to assess the variability of discharge of these organic compounds under a rigid QA/QC program.

In addition, unspecified alkyl benzenes were detected in both the base-neutral and volatile analytical groups, and alkylated phenols on the acid fraction as well as phenol itself. It was noted that, for intermediate treatment wastes, there was good agreement between the 4 amino-anti-pyrine colorimetric test and the (much more expensive) GC/MS analyses.

A PACE report entitled "Evaluation of the Variability of Trace Organic Substances in Petroleum Refinery Effluents"(17), examined the variability of contaminant discharge from a single refinery. Fifteen intake and 15 final effluent samples were collected over a period of two months. They were analyzed using 1979 U.S. EPA priority pollutant protocols. Quality control measures applied the experience of modern analytical approaches using deuterium labelled priority pollutants.

Substances found in the effluents at statistically higher concentrations were ammonia, total phenolics, dimethyl naphthalene, phenanthrene, dimethylphenol, naphthalene and 1-methylcyclopentane. Ethylbenzene and chrysenes were at higher concentrations in intake water.

Other noteworthy findings were that:

- variability in effluent concentrations and intake waters was significantly greater than analytical variability. It was concluded that process and environmental variations could not be solely attributed to analytical variability;

- no clear relationship between conventional parameters and trace organic compounds could be observed;

- the total discharge of organic priority pollutants was less than 1 kg/day.

This information base has been further summarized and reviewed in the report "A Survey of Trace Substances in Canadian Oil Refinery Wastewaters and Sludges--A Summary Report"(22).

The historical PACE and OPA data were reviewed for the Joint Technical Committee during development of the draft regulation in a report entitled: "Environmental Contaminants in Petroleum Refinery Wastewaters: An Assessment of Current Information and a Monitoring Approach"(23).

This report summarizes the findings of an Industry-Government Trace Contaminants Working Group which reviewed the chemical studies on trace contaminants in refinery effluent and reported agreements with and objections to the Effluent Monitoring Regulation.

The Working Group accepted the premise for regulatory (uniform and consistent) monitoring for all Sectors and the concept of monitoring trace contaminants at the undiluted process effluent sampling point.

The summary statement was that "under good operating conditions" the treated effluents from Ontario petroleum refineries contain only a few trace contaminants and their concentrations are consistently less than 50 parts per billion.

The Working Group endorsed, with reservations, the low-frequency characterization regulatory monitoring approach for the EMPPL-based list but noted that a series of wastewater development studies should be done as well in logical, step-wise fashion.

The pollutants required under regulation to be monitored daily were endorsed with the note that additional monitoring "including (perhaps) organic carbon" were already used by the refineries to demonstrate consistent operation. They noted the utility of dissolved oxygen uptake rate and a number of other aeration basin parameters (which are outside the scope of the regulation).

Pollutants proposed to be monitored on a three times weekly basis were endorsed in that the Working Group agreed that the parameters "should be monitored on a frequency of more than monthly but less than daily"; specifically the pollutants were:

- volatiles (benzene, toluene, xylene, ethylbenzene: indicator priority pollutants);
- oil and grease;
- ammonia nitrogen.

Frequent monitoring for zinc, chromium, or phosphorus, when used, was recommended.

The Working Group did not agree on the need for monitoring 12 times a year and did not agree on the Ministry decision to base the monitoring list on intermediate wastewaters. The industry representatives felt that the existing effluent quality data base should have been the decisive factor. There was agreement that biological treatment was critical for priority pollutant abatement. Further recommendations were that:

- a listing/de-listing mechanism should be written into the regulation;
- results should be made public within four weeks of receipt.

Pre-regulatory Monitoring

A supplementary study, "Sampling and Analysis of Refinery Effluents to Assess Variations in Trace Contaminant Concentrations" (18), was completed during the pre-regulatory period. Effluent variability at two Ontario refineries was studied under the supervision of the Joint Government-Industry Technical Committee for the Petroleum Refining sector.

Phthalate esters were detected in more than fifty percent of all effluents, but were also found in field blanks. The report noted the ubiquitous nature of these plasticizers. Volatile aromatics were detected at medium frequency in effluents from one refinery but not the other. PAHs were detected in intermediate wastewaters but were reduced in final effluents to the point of non-detection in one refinery; dimethyl and tri-methyl naphthalene were detected at medium frequency in effluents from the other refinery.

Toxicity Studies

The sub-lethal (and lethal) toxicity of refinery effluents was addressed in a report entitled "Sub-lethal Effects of Treated Liquid Effluent From a Petroleum Refinery on Freshwater Organisms" (24) provided by PACE with assistance from Environment Canada.

The Abstract of that report noted that:

> "Over two years, 71 of 94 effluent samples met federal guidelines for non-lethality to trout."

Several sub-lethal studies were conducted in addition to lethality tests and the results reported. Of greatest interest for regulatory purposes, however, were the findings of the water flea studies which used *Daphnia pulex* (de Geer) rather than *Daphnia magna*, due to the observation, at that time, that *Daphnia magna* are less widespread in Canadian waters and have longer development times.

The summary conclusions for the lethal tests from the body of the report are reproduced here for convenience:

> "To summarize, the 48-hour lethal test with *Daphnia pulex* is a useful one in many respects:
>
> (a) For monitoring, it is small-scale, simple, inexpensive, sensitive, and relatively fast.
>
> (b) It requires only small volumes of effluent, a useful feature for shipping from remote areas and for evaluating pilot-plant effluents.

(c) It could be adopted as a standard test, or used to predict the mortality of trout.

(d) The acute test could predict sub-lethal effects on Daphnia, by using the factor 0.41 to estimate median effective concentration for reproductive inhibition, or by using the application factor 0.0068 to predict "safe" levels for Daphnia.

(e) The acute test with Daphnia could also predict sub-lethal effects on fish. Multiplying the Daphnia 0.13 yields the sub-lethal threshold for growth of trout."

In the abstract, it was noted that:

> "Daphnia pulex were killed in two days by 76% effluent and were 2.5 times as sensitive as trout".

The final summary sentence from the Abstract noted:

> "Two day lethal tests with Daphnia pulex would seem to be useful as rapid assays for monitoring or screening refinery effluents."

The results of the more complex sub-lethal tests are best understood by direct reference to the text of this exhaustive report.

The toxicity and carcinogenicity of refinery effluents have also been studied and reported by PACE in their report, number 85-4, entitled "The Investigation of the Potential Carcinogenic Activity of Oil Refinery Effluents" (25), dated December 1985. In that report Professor Sonstegard of McMaster University evaluated the mutagenic and carcinogenic potential of refinery effluents. The report noted that no evidence of carcinogenic potential was detected in a trout embryo carcinogenesis bioassay using concentrated refinery effluents alone. There was some evidence that refinery effluent extract, when co-injected with one potent carcinogen, could result in increased tumour incidence. The co-injection of another carcinogen did not produce similar results and the authors concluded that the combined effects were specific to certain interactions which might be 'useful although difficult' to associate with specific compounds in the effluent.

A standard test for mutagenicity (Ames test) indicated that the concentrated extracts of refinery effluents showed low mutagenic activity, lower than the genotoxic activity for municipal drinking water of several Canadian cities.

The introduction to the report noted that crude oil contains polynuclear aromatic hydrocarbons (PAHs), which are present therefore in the low ppb range in refinery effluents. There is some evidence that the methylated PAHs likely to be present in refinery effluents are more carcinogenic than their non-methylated parent compounds but little is actually known about their carcinogenicity related to chemical composition. The other potentially carcinogenic compounds in refinery effluents cited in the introduction were benzene, a recognized leukemia-causing agent in humans, and alkyl halides which have been reported by PACE in effluents.

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